

Supplementary Information

A general Fe-catalysed azidation of iododifluoroketones and its utilization for synthesis of *gem*-difluoromethylenated triazoles

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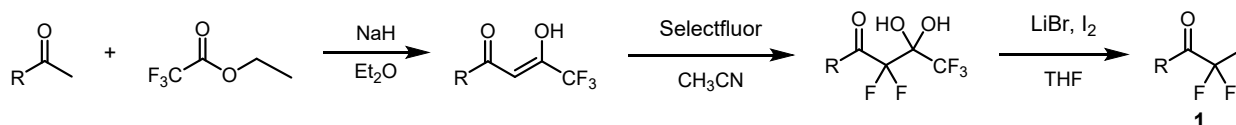
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Instrumentation and Chemicals

^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were recorded at 400 MHz, 100 MHz, and 376 MHz, respectively, for CDCl_3 solutions. High-resolution mass spectra (HRMS) were recorded on a FTMS instrument in ESI mode and reported as m/z . Melting points were obtained on digital melting point apparatus without correction. Unless otherwise stated, all reagents were commercially purchased and used without further purification. Substrates **1t** and **3f** was synthesized according to procedures reported previously.^[S1]

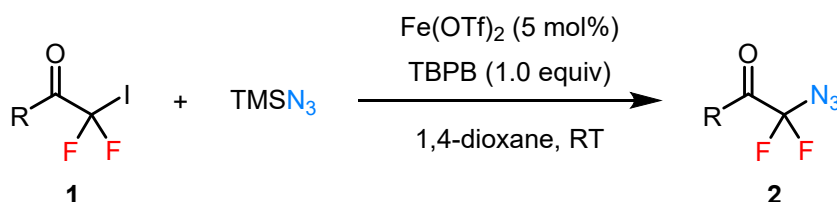
Experimental Procedures

1. Preparation of 2-iodo-2,2-difluoroacetophenone 1a-1r



The 2-iodo-2,2-difluoroacetophenone **1a-1r** were prepared according to the reported procedure.^[S2] They are all known compounds. As shown above, the intermediates enols were obtained from the reaction of ethyl 2,2,2-trifluoroacetate and ketones. The enols reacted with Selectfluor to form fluorinated *gem*-diols, which then reacted with I₂ to afford 2-iodo-2,2-difluoroacetophenone **1a-1r** using the trifluoroacetate release conditions.

2. Procedure for iron-catalysed azidation of iododifluoroketones (Scheme 2)

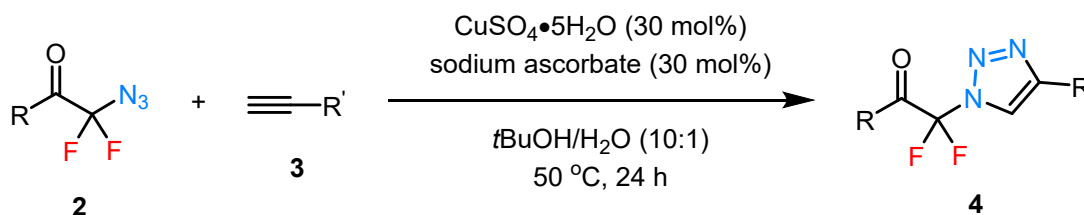


An oven-dried tube was charged with Fe(OTf)₂ (0.01 mmol, 5 mol%). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, 2-iodo-2,2-difluoroacetophenone derivatives **1** (0.2 mmol) dissolved in 1,4-dioxane (2.0 mL), TMSN₃ (0.24 mmol, 1.2 equiv) and TBPB (0.2 mmol, 1.0 equiv) were added into the tube under the protection of nitrogen. The reaction mixture was stirring at 25 °C for 12 h. After the reaction was completed, evaporation of the solvent was performed on a rotary evaporator, and the reaction mixture was added directly to a column loaded with silica gel pre-eluted with the mobile phase solvent system (petroleum ether/ethyl acetate, 100:1). Chromatography afforded the desired products **2a-2r**.

A 4.0 mmol scale reaction of 1a (Scheme 4a): An oven-dried tube was charged with Fe(OTf)₂ (0.2 mmol, 5mol %). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, 2-iodo-2,2-difluoroacetophenone derivatives **1** (4.0 mmol) dissolved in 1,4-dioxane (30 mL), TMSN₃ (4.8 mmol, 1.2 equiv) and TBPB (4.0 mmol, 1.0 equiv) were added into the tube under the protection of nitrogen. The reaction mixture was stirring at 25 °C for 12 h. After the reaction was completed, evaporation of the solvent was performed on a rotary evaporator, and the reaction mixture was added directly to a column loaded with silica gel pre-eluted with the mobile phase solvent system (petroleum ether/ethyl acetate, 100:1). Chromatography afforded the desired product **2a** (81%, 640.0

mg).

3. Procedure for the synthesis of *gem*-difluoromethylenated triazoles (Scheme 3)



An oven-dried tube was charged with CuSO₄·5H₂O (0.06 mmol, 30 mol%), sodium ascorbate (0.06 mmol, 30 mol%), and *tert*-butanol/water (10:1, 2.0 mL in total). The azidation product **2** (0.2 mmol) and alkynes **3** (0.22 mmol, 1.1 equiv) were sequentially added to the same reaction vessel, and the mixture was left to stir for 24 h at 50 °C (reaction monitored by TLC following the consumption of azide and appearance of triazole using petroleum ether/ethyl acetate, 5:1). Upon completion, the reaction mixture was added directly to a column loaded with silica gel pre-eluted with the mobile phase solvent system (petroleum ether/ethyl acetate, 5:1). Chromatography afforded the desired triazole products **4**.

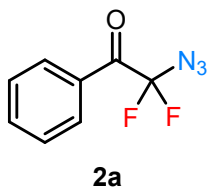
4. One-pot, two-step procedure for the synthesis of *gem*-difluoromethylenated triazoles (Scheme 4b)

An oven-dried tube was charged with Fe(OTf)₂ (0.01 mmol, 5 mol%). The tube was evacuated and backfilled with nitrogen (repeated three times). Then, 2-iodo-2,2-difluoroacetophenone derivatives **1** (0.2 mmol) dissolved in 1,4-dioxane (2.0 mL), TMSN₃ (0.24 mmol, 1.2 equiv) and TBPB (0.2 mmol, 1.0 equiv) were added into the tube under the protection of nitrogen. The reaction mixture was stirring at 25 °C for 12 h. After the reaction was completed, evaporation of the solvent was performed on a rotary evaporator, followed by the addition of *tert*-butanol/water (10:1, 2.0 mL in total), alkyne (0.22 mmol), CuSO₄·5H₂O (0.06 mmol, 30 mol%), and sodium ascorbate (0.06 mmol, 30 mol%) to the same reaction vessel, and the mixture was left to stir for 24 h at 50 °C (reaction monitored by TLC following the consumption of azide and appearance of triazole using petroleum ether/ethyl acetate, 5:1). Upon completion, the reaction mixture was added directly to a column loaded with silica gel pre-eluted with the mobile phase solvent system (petroleum ether/ethyl acetate, 5:1). Chromatography afforded the desired triazole products **4**.

Characterization Data for Substrates and Products

^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra for all compounds are attached in the last part.

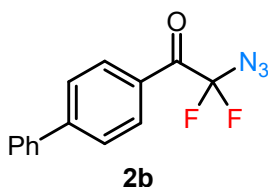
The characterization data for **2a** and **2l** are consistent with that reported in previous work.^[S3,S4]



2-Azido-2,2-difluoro-1-phenylethan-1-one (**2a**)

Colorless oil (96%), purified by silica-gel column chromatography (PE/EA).

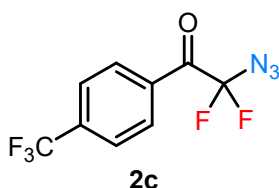
^1H NMR (400 MHz, CDCl_3): δ 8.10 (d, $J = 8.0$ Hz, 2H), 7.69 (t, $J = 8.0$ Hz, 1H), 7.53 (t, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 183.25 (t, $^2J_{\text{C-F}} = 34.0$ Hz), 135.17, 130.42 (t, $^3J = 3.0$ Hz), 128.91, 128.57, 115.47 (t, $^1J = 272.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3): δ -78.02 (s, 2F).



1-([1,1'-Biphenyl]-4-yl)-2-azido-2,2-difluoroethan-1-one (**2b**)

Colorless oil (92%), purified by silica-gel column chromatography (PE/EA).

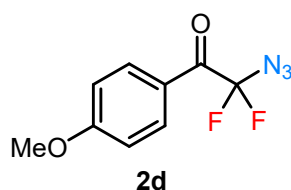
^1H NMR (400 MHz, CDCl_3): δ 8.19 (d, $J = 8.0$ Hz, 2H), 7.76 (d, $J = 12.0$ Hz, 2H), 7.67-7.64 (m, 2H), 7.53-7.43 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 182.85 (t, $^2J_{\text{C-F}} = 34.0$ Hz), 147.93, 139.29, 131.12 (t, $^3J_{\text{C-F}} = 2.5$ Hz), 129.18, 129.05, 128.90, 127.51, 127.41, 115.68 (t, $^1J_{\text{C-F}} = 271.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3): δ -77.88 (s, 2F). HRMS (ESI) m/z calcd $[\text{M} + \text{H}]^+$ = for $\text{C}_{14}\text{H}_9\text{F}_2\text{N}_3\text{O}$: 274.0792, found: 274.0800.



2-Azido-2,2-difluoro-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**2c**)

Colorless oil (99%), purified by silica-gel column chromatography (PE/EA).

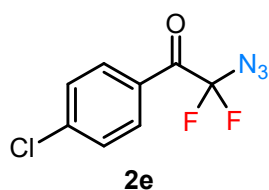
^1H NMR (400 MHz, CDCl_3): δ 8.20 (p, $J = 8.0$ Hz, 2H), 7.79 (p, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 182.46 (t, $^2J_{\text{C-F}} = 35.0$ Hz), 136.36 (q, $^2J_{\text{C-F}} = 32.7$ Hz), 133.07, 130.72, 125.91 (t, $^3J_{\text{C-F}} = 4.0$ Hz), 124.58 (q, $^1J_{\text{C-F}} = 295.3$ Hz), 115.16 (t, $^1J_{\text{C-F}} = 272.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3): δ -63.68 (s, 3F), -78.36 (s, 2F). HRMS (ESI) m/z calcd $[\text{M} + \text{H}]^+$ = for $\text{C}_9\text{H}_4\text{F}_5\text{N}_3\text{O}$: 266.0353, found: 266.0358.



2-Azido-2,2-difluoro-1-(4-methoxyphenyl)ethan-1-one (2d)

Colorless oil (82%), purified by silica-gel column chromatography (PE/EA).

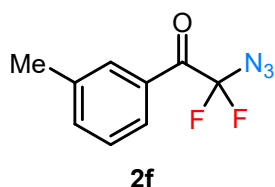
¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, *J* = 8.0 Hz, 2H), 6.98-6.94 (m, 2H), 3.88 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ 181.64 (t, ²*J*_{C-F} = 32.5 Hz), 165.25, 133.06 (t, ³*J*_{C-F} = 3.0 Hz), 123.08, 115.79 (t, ¹*J*_{C-F} = 271.0 Hz), 114.30, 55.66. **¹⁹F NMR** (376 MHz, CDCl₃): δ -77.63 (s, 2F). **HRMS (ESI)** *m/z* calcd [M + H]⁺ = for C₉H₇F₂N₃O₂: 228.0585, found: 228.0591.



2-Azido-1-(4-chlorophenyl)-2,2-difluoroethan-1-one (2e)

Colorless oil (84%), purified by silica-gel column chromatography (PE/EA).

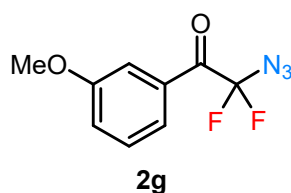
¹H NMR (400 MHz, CDCl₃): δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H). **¹³C NMR** (100 MHz, CDCl₃): δ 182.18 (t, ²*J*_{C-F} = 34.0 Hz), 142.12, 131.81 (t, ³*J*_{C-F} = 3.0 Hz), 129.40, 128.65, 115.37 (t, ¹*J*_{C-F} = 271.0 Hz). **¹⁹F NMR** (376 MHz, CDCl₃): δ -77.98 (s, 2F). **HRMS (ESI)** *m/z* calcd [M + Na]⁺ = for C₈H₄ClF₂N₃O: 253.9909, found: 253.9913.



2-Azido-2,2-difluoro-1-(*m*-tolyl)ethan-1-one (2f)

Colorless oil (85%), purified by silica-gel column chromatography (PE/EA).

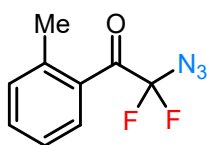
¹H NMR (400 MHz, CDCl₃): δ 7.89 (s, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.43-7.37 (m, 1H), 2.42 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ 183.40 (t, ²*J*_{C-F} = 33.5 Hz), 138.93, 136.06, 130.77, 130.38, 128.78, 127.69 (t, ³*J*_{C-F} = 3.0 Hz), 115.57 (t, ¹*J*_{C-F} = 271.5 Hz), 21.26. **¹⁹F NMR** (376 MHz, CDCl₃): δ -78.03 (s, 2F). **HRMS (ESI)** *m/z* calcd [M + Na]⁺ = for C₉H₇F₂N₃O: 234.0455, found: 234.0457.



2-Azido-2,2-difluoro-1-(3-methoxyphenyl)ethan-1-one (2g)

Colorless oil (91%), purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.45-7.40 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ 183.12 (t, ²*J*_{C-F} = 34.0 Hz), 159.90, 131.52, 129.96, 123.09 (t, ³*J*_{C-F} = 3.5 Hz), 121.90, 115.48 (t, ¹*J*_{C-F} = 272.0 Hz), 114.46, 55.55. **¹⁹F NMR** (376 MHz, CDCl₃): δ -77.86 (s, 2F). **HRMS (ESI)** *m/z* calcd [M + H]⁺ = for C₉H₇F₂N₃O₂: 228.0585, found: 228.0583.

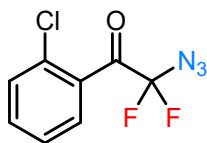


2h

2-Azido-2,2-difluoro-1-(*o*-tolyl)ethan-1-one (2h)

Colorless oil (94%), purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.34-7.30 (m, 2H), 2.54 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃): δ 186.00 (t, ²*J*_{C-F} = 36.0 Hz), 141.59, 133.57, 132.43, 130.39, 130.14, 125.78, 115.12 (t, ¹*J*_{C-F} = 272.5 Hz), 21.55. **¹⁹F NMR** (376 MHz, CDCl₃): δ -78.61 (s, 2F). **HRMS (ESI)** *m/z* calcd [M + H]⁺ = for C₉H₇F₂N₃O: 212.0635, found: 212.0628.

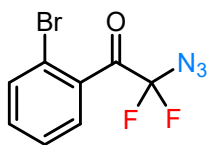


2i

2-Azido-1-(2-chlorophenyl)-2,2-difluoroethan-1-one (2i)

Colorless oil (83%), purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.40-7.33 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃): δ 185.51 (t, ²*J*_{C-F} = 36.0 Hz), 134.57, 132.20, 131.52, 130.69, 129.08, 127.58, 114.28 (t, ¹*J*_{C-F} = 272.0 Hz). **¹⁹F NMR** (376 MHz, CDCl₃): δ -80.67 (s, 2H). **HRMS (ESI)** *m/z* calcd [M + Na]⁺ = for C₈H₄ClF₂N₃O: 253.9909, found: 253.9907.



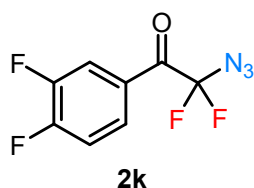
2j

2-Azido-1-(2-bromophenyl)-2,2-difluoroethan-1-one (2j)

Colorless oil (90%), purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃): δ 7.72-7.69 (m, 1H), 7.65-7.62 (m, 1H), 7.45-7.39 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃): δ 186.15 (t, ²*J*_{C-F} = 38.5 Hz), 134.57, 133.58, 134.42, 129.71 (t, ³*J*_{C-F} = 3.0 Hz), 127.23, 121.19, 114.09 (t, ¹*J*_{C-F} = 271.5 Hz). **¹⁹F NMR** (376 MHz, CDCl₃): δ -80.58 (s, 2F). **HRMS**

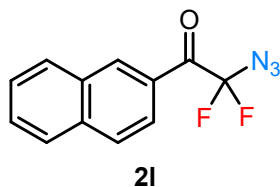
(ESI) m/z calcd $[M + Na]^+$ = for $C_8H_4BrF_2N_3O$: 297.9404, found: 297.9410.



2-Azido-1-(3,4-difluorophenyl)-2,2-difluoroethan-1-one (2k)

Colorless oil (97%), purified by silica-gel column chromatography (PE/EA).

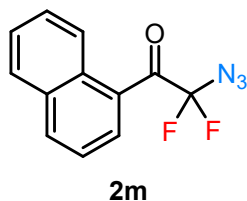
1H NMR (400 MHz, $CDCl_3$): δ 8.15-7.99 (m, 2H), 7.54-7.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.13 (t, $^2J_{C-F}$ = 23.5 Hz), 156.13 (d, $^1J_{C-F}$ = 256.0 Hz), 151.60 (d, $^1J_{C-F}$ = 250.0 Hz), 128.32, 125.23, 120.38 (d, $^2J_{C-F}$ = 18.0 Hz), 118.15 (dd, $^2J_{C-F}$ = 18.0, 11.0 Hz), 94.75 (t, $^2J_{C-F}$ = 325.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -54.63 (s, 2F), -124.86 (dd, J = 18.8, 7.5 Hz), -134.12 (dd, J = 18.8, 7.5 Hz). HRMS (ESI) m/z calcd $[M + H]^+$ = for $C_8H_3F_4N_3O$: 234.0290, found: 234.0285.



2-Azido-2,2-difluoro-1-(naphthalen-2-yl)ethan-1-one (2l)

Colorless oil (95%), purified by silica-gel column chromatography (PE/EA).

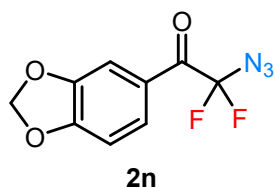
1H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 6.0 Hz, 1H), 7.58 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.24 (t, $^2J_{C-F}$ = 34.0 Hz), 136.40, 133.48 (t, $^3J_{C-F}$ = 3.5 Hz), 132.23, 130.24, 129.93, 128.91, 127.92, 127.58, 127.34, 124.65, 115.78 (t, $^1J_{C-F}$ = 271.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -77.25 (s, 2F).



2-Azido-2,2-difluoro-1-(naphthalen-1-yl)ethan-1-one (2m)

Colorless oil (92%), purified by silica-gel column chromatography (PE/EA).

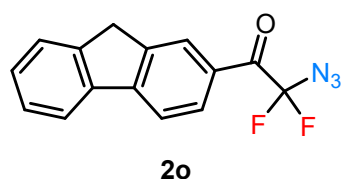
1H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 6.0 Hz, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.51 (t, J = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.97 (t, $^2J_{C-F}$ = 33.0 Hz), 135.57, 134.00, 131.29 (t, $^3J_{C-F}$ = 4.5 Hz), 131.20, 129.20, 129.02, 127.31, 127.05, 125.20, 124.13, 115.37 (t, $^1J_{C-F}$ = 273.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -77.55 (s, 2F). HRMS (ESI) m/z calcd $[M + Na]^+$ = for $C_{12}H_7F_2N_3O$: 270.0455, found: 270.0454.



2-Azido-1-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoroethan-1-one (2n)

Colorless oil (77%), purified by silica-gel column chromatography (PE/EA).

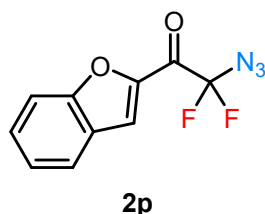
¹H NMR (400 MHz, CDCl₃): δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.46 (s, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 2H). **¹³C NMR** (100 MHz, CDCl₃): δ 181.26 (t, ²*J*_{C-F} = 33.5 Hz), 153.78, 148.42, 127.91 (t, ³*J*_{C-F} = 3.5 Hz), 124.59, 115.68 (t, ¹*J*_{C-F} = 271.0 Hz), 109.57, 108.38, 102.47. **¹⁹F NMR** (376 MHz, CDCl₃): δ -77.27 (s, 2F). **HRMS (ESI)** *m/z* calcd [M + H]⁺ = for C₉H₅F₂N₃O₃: 242.0377, found: 242.0372.



2-Azido-1-(9H-fluoren-2-yl)-2,2-difluoroethan-1-one (2o)

Colorless oil (82%), purified by silica-gel column chromatography (PE/EA).

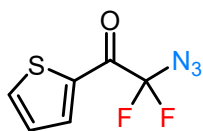
¹H NMR (400 MHz, CDCl₃): δ 8.22 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.84-7.80 (m, 2H), 7.59-7.57 (m, 1H), 7.43-7.41 (m, 2H), 3.90 (s, 2H). **¹³C NMR** (100 MHz, CDCl₃): δ 182.96 (t, ²*J*_{C-F} = 33.5 Hz), 148.62, 144.96, 143.46, 139.95, 129.99 (t, ³*J*_{C-F} = 3.0 Hz), 128.90, 128.44, 127.33, 127.02 (t, ⁴*J*_{C-F} = 2.5 Hz), 125.40, 121.40, 120.01, 115.85 (t, ¹*J*_{C-F} = 271.5 Hz), 36.89. **¹⁹F NMR** (376 MHz, CDCl₃): δ -77.35 (s, 2F). **HRMS (ESI)** *m/z* calcd [M + Na]⁺ = for C₁₅H₉F₂N₃O: 308.0611, found: 308.0609.



2-Azido-1-(benzofuran-2-yl)-2,2-difluoroethan-1-one (2p)

Colorless oil (63%), purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃): δ 7.86 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.65-7.55 (m, 2H), 7.40-7.35 (m, 1H). **¹³C NMR** (100 MHz, CDCl₃): δ 173.57, 156.76, 146.57, 130.46, 126.54, 124.77, 124.25, 120.34, 114.82, 112.79. **¹⁹F NMR** (376 MHz, CDCl₃): δ -79.87 (s, 2F). **HRMS (ESI)** *m/z* calcd [M + Na]⁺ = for C₁₀H₅F₂N₃O₂: 260.0242, found: 260.0249.

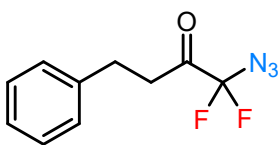


2q

2-Azido-2,2-difluoro-1-(thiophen-2-yl)ethan-1-one (2q)

Colorless oil (86%), purified by silica-gel column chromatography (PE/EA).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.00 (d, $J = 4.0$ Hz, 1H), 7.88 (d, $J = 4.0$ Hz, 1H), 7.22 (t, $J = 6.0$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 176.63 (t, $^2J_{\text{C-F}} = 35.5$ Hz), 137.92, 136.88 (t, $^3J_{\text{C-F}} = 4.0$ Hz), 136.36, 129.13, 115.14 (t, $^1J_{\text{C-F}} = 270.0$ Hz). $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -78.89 (s, 2F). **HRMS (ESI)** m/z calcd $[\text{M} + \text{Na}]^+$ = for $\text{C}_6\text{H}_3\text{F}_2\text{N}_3\text{OS}$: 225.9863, found: 225.9867.

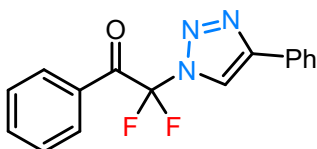


2r

1-Azido-1,1-difluoro-4-phenylbutan-2-one (2r)

Colorless oil (71%), purified by silica-gel column chromatography (PE/EA).

$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.30-7.27 (m, 2H), 7.22-7.16 (m, 3H), 3.15-2.92 (m, 4H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 193.81 (t, $^2J_{\text{C-F}} = 34.5$ Hz), 139.61, 128.79, 128.38, 126.69, 114.09 (t, $^1J_{\text{C-F}} = 271.0$ Hz), 37.89, 28.60. $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -85.58 (s, 2F). **HRMS (ESI)** m/z calcd $[\text{M} + \text{H}]^+$ = for $\text{C}_{10}\text{H}_9\text{F}_2\text{N}_3\text{O}$: 226.0792, found: 226.0792.

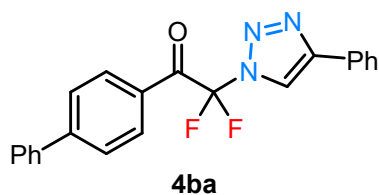


4aa

2,2-Difluoro-1-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4aa)

White solid (95%), m.p. = 97.2 °C, purified by silica-gel column chromatography (PE/EA).

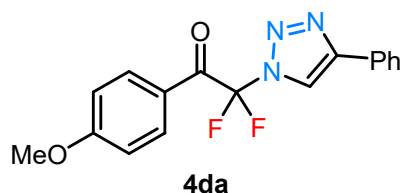
$^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.29 (s, 1H), 8.03 (d, $J = 8.0$ Hz, 2H), 7.90 (d, $J = 8.0$ Hz, 2H), 7.68 (t, $J = 6.0$ Hz, 1H), 7.52-7.45 (m, 4H), 7.40 (t, $J = 6.0$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 181.76 (t, $^2J_{\text{C-F}} = 29.5$ Hz), 148.71, 135.31, 130.95 (t, $^3J_{\text{C-F}} = 3.0$ Hz), 130.37, 129.20, 129.07, 129.03, 128.95, 126.16, 117.20, 111.72 (t, $^1J_{\text{C-F}} = 268.0$ Hz). $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -82.29 (s, 2F). **HRMS (ESI)** m/z calcd $[\text{M} + \text{CH}_3\text{OH} + \text{H}]^+$ = for $\text{C}_{16}\text{H}_{11}\text{F}_2\text{N}_3\text{O}$: 332.1205, found: 332.1208.



1-([1,1'-Biphenyl]-4-yl)-2,2-difluoro-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4ba)

White solid (78%), m.p. = 140.6 °C, purified by silica-gel column chromatography (PE/EA).

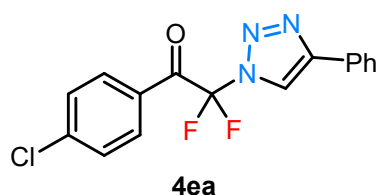
¹H NMR (500 MHz, CDCl₃): δ 8.34 (s, 1H), 8.11 (d, *J* = 10 Hz, 2H), 7.92 (d, *J* = 5 Hz, 2H), 7.71 (d, *J* = 5 Hz, 2H), 7.63 (d, *J* = 10 Hz, 2H), 7.50-7.41 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 181.29 (t, ²*J*_{C-F} = 27.5 Hz), 148.75, 148.01, 139.14, 131.06, 129.55, 129.23, 129.15, 129.10, 128.98, 128.91, 127.59, 127.39, 126.18, 117.35, 111.81 (¹*J*_{C-F} = 267.5 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -81.59 (s, 2F). HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₂₂H₁₅F₂N₃O: 398.1081, found: 398.1082.



2,2-Difluoro-1-(4-methoxyphenyl)-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4da)

White solid (54%), m.p. = 88.0 °C, purified by silica-gel column chromatography (PE/EA).

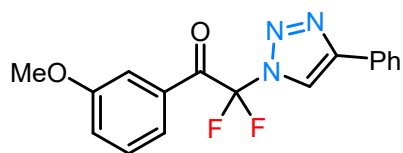
¹H NMR (500 MHz, CDCl₃): δ 8.28 (s, 1H), 8.01 (d, *J* = 10 Hz, 2H), 7.88 (d, *J* = 5.0 Hz, 2H), 7.44 (t, *J* = 10 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 5 Hz, 2H), 3.85 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 180.07 (t, ²*J*_{C-F} = 30.0 Hz), 165.33, 148.58, 133.08, 129.13, 129.05, 126.12, 125.86, 123.60, 117.42, 114.45, 111.98 (¹*J*_{C-F} = 270 Hz), 55.70. ¹⁹F NMR (376 MHz, CDCl₃): δ -81.25 (s, 2F). HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₁₇H₁₃F₂N₃O₂: 352.0874, found: 352.0865.



1-(4-Chlorophenyl)-2,2-difluoro-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4ea)

White solid (64%), m.p. = 104.2 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 4.0 Hz, 2H), 7.46-7.42 (m, 4H), 7.40-7.37(m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 180.80 (t, ²*J*_{C-F} = 29.5 Hz), 148.86, 142.25, 131.78, 131.75, 129.52, 129.33, 129.13, 128.83, 126.19, 117.36, 111.61 (t, ¹*J*_{C-F} = 268.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -82.20 (s, 2F). HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₁₆H₁₀ClF₂N₃O: 356.0378, found: 356.0371.

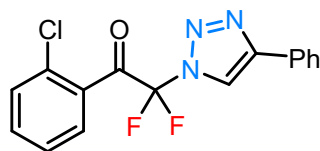


4ga

2,2-Difluoro-1-(3-methoxyphenyl)-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4ga)

White solid (89%), m.p. = 95.2 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃) δ 8.32 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.55-7.51 (m, 2H), 7.46-7.33 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 181.55 (t, ²*J*_{C-F} = 29.5 Hz), 159.92, 148.74, 131.99, 130.12, 129.26, 129.12, 128.93, 126.18, 122.93 (t, ²*J*_{C-F} = 3.5 Hz), 122.02, 117.37, 114.52, 111.72 (t, ¹*J*_{C-F} = 267.5 Hz), 55.58. ¹⁹F NMR (376 MHz, CDCl₃) δ -82.04 (s, 2F). HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₁₇H₁₃F₂N₃O₂: 352.0874, found: 352.0874.

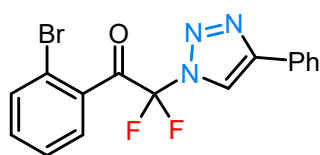


4ia

1-(2-Chlorophenyl)-2,2-difluoro-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4ia)

White solid (51%), m.p. = 68.4 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 1H) 7.89 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.54-7.44 (m, 4H), 7.41-7.34 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 184.26 (t, ²*J*_{C-F} = 32.0 Hz), 148.65, 133.82, 133.48, 131.80, 131.26, 130.27, 129.28, 129.14, 128.91, 126.89, 126.19, 117.72, 110.92 (t, ¹*J*_{C-F} = 269.5). ¹⁹F NMR (376 MHz, CDCl₃) δ -84.77 (s, 2F). HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₁₆H₁₀ClF₂N₃O: 356.0378, found: 356.0373.

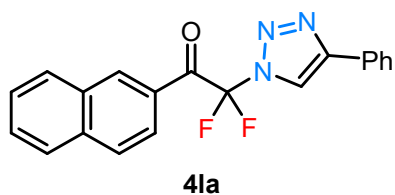


4ja

1-(2-Bromophenyl)-2,2-difluoro-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4ja)

White solid (63%), m.p. = 78.6 °C, purified by silica-gel column chromatography (PE/EA).

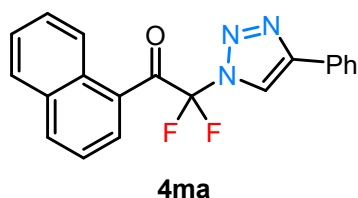
¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2 H) 7.72-7.68 (m, 2H), 7.47-7.37 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 185.00, 148.65, 134.47, 133.79, 133.73, 130.17, 129.30, 129.15, 128.88, 127.42, 126.20, 121.24, 117.78, 110.76 (t, ¹*J*_{C-F} = 269.5 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -84.72 (s, 2F). HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₁₆H₁₀BrF₂N₃O: 399.9873, found: 399.9869.



2,2-Difluoro-1-(naphthalen-2-yl)-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4la)

White solid (87%), m.p. = 126.4 °C, purified by silica-gel column chromatography (PE/EA).

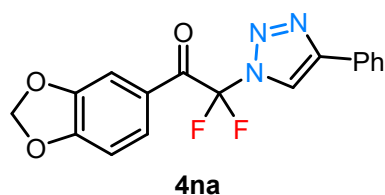
¹H NMR (500 MHz, CDCl₃): δ 8.60 (s, 1H), 8.34 (s, 1H), 8.02 (s, 1H), 7.95-7.85 (m, 5H), 7.64 (s, 1H), 7.57 (s, 1H), 7.47-7.39 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 181.78 (t, ²J_{C-F} = 30.0 Hz), 148.72, 136.38, 133.50, 132.18, 130.29, 130.06, 129.20, 129.08, 129.02, 128.98, 128.17, 127.88, 127.38, 126.17, 124.56, 117.42, 111.99 (t, ¹J_{C-F} = 268.1 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -81.03 (s, 2F). **HRMS (ESI)** m/z calcd [M + Na]⁺ = for C₂₀H₁₃F₂N₃O: 372.0924, found: 372.0916.



2,2-Difluoro-1-(naphthalen-1-yl)-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4ma)

White solid (72%), m.p. = 99.4 °C, purified by silica-gel column chromatography (PE/EA).

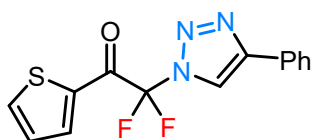
¹H NMR (500 MHz, CDCl₃): δ 8.72 (d, *J* = 10.0 Hz, 1H), 8.33 (s, 1H), 8.12-8.08 (m, 2H), 7.91-7.89 (m, 3H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.51-7.38 (m, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 184.16 (t, ²J_{C-F} = 29.4 Hz), 148.57, 135.67, 133.96, 131.16, 129.33, 129.16, 129.15, 129.07, 129.03, 128.97, 127.78, 127.15, 126.15, 125.23, 124.12, 117.74, 111.76 (t, ¹J_{C-F} = 270.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃): δ -80.99 (s, 2F). **HRMS (ESI)** m/z calcd [M + Na]⁺ = for C₂₀H₁₃F₂N₃O: 372.0924, found: 372.0923.



1-(Benzo[*d*][1,3]dioxol-5-yl)-2,2-difluoro-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one (4na)

White solid (43%), m.p. = 86.1 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.49-7.43 (m, 3H), 7.40-7.37 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.06 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 179.77 (t, ²J_{C-F} = 29.0 Hz), 153.95, 148.67, 148.55, 129.22, 129.11, 128.99, 128.03 (t, ³J_{C-F} = 3.5 Hz), 126.17, 125.25, 117.41, 111.91 (t, ¹J_{C-F} = 269.5 Hz), 109.66, 108.59, 102.54. ¹⁹F NMR (376 MHz, CDCl₃) δ -81.59 (s, 2F). **HRMS (ESI)** m/z calcd [M + Na]⁺ = for C₁₇H₁₁F₂N₃O₃: 366.0666, found: 366.0663.



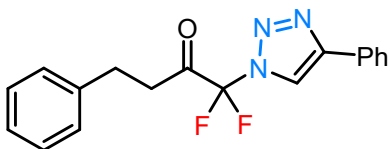
4qa

2,2-Difluoro-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-1-(thiophen-2-yl)ethan-1-one (4qa)

White solid (62%), m.p. = 145.2 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (500 MHz, CDCl₃): δ 8.28 (s, 1H), 7.95 (s, 1H), 7.88-7.86 (m, 3H), 7.44 (dt, *J* = 30.0, 10.0 Hz, 3H), 7.19 (t, *J* = 5.0 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 174.91 (t, ²*J*_{C-F} = 32.5 Hz), 148.57, 138.37, 137.05, 136.75, 129.32, 129.18, 129.06, 128.94, 126.14, 117.55, 111.54 (t, ¹*J*_{C-F} = 267.5 Hz).

¹⁹F NMR (376 MHz, CDCl₃): δ -82.81 (s, 2F). HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₁₄H₉F₂N₃OS: 328.0332, found: 328.0329.



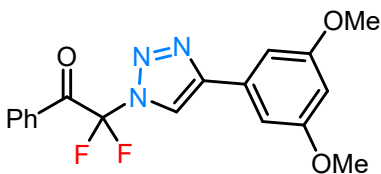
4ra

1,1-Difluoro-4-phenyl-1-(4-phenyl-1*H*-1,2,3-triazol-1-yl)butan-2-one (4ra)

White solid (45%), m.p. = 70.6 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (500 MHz, CDCl₃): δ 8.13-8.11 (m, 2H), 7.85 (d, *J* = 10 Hz, 1H), 7.60 (t, *J* = 10 Hz, 1H), 7.46 (q, *J* = 10 Hz, 3H), 7.40-7.37 (m, 1H), 7.29 (t, *J* = 10 Hz, 1H), 7.24-7.19 (m, 2H), 3.28 (t, *J* = 10 Hz, 2H), 3.06 (t, *J* = 10 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 192.04 (t, ²*J*_{C-F} = 30.0 Hz), 172.09, 148.60, 139.43, 133.82, 130.24, 129.42, 129.26, 129.10, 128.73, 128.53, 128.38, 126.65, 126.17, 117.36, 110.52 (¹*J*_{C-F} = 267.5 Hz), 39.42, 28.73. ¹⁹F NMR (376 MHz, CDCl₃): δ -95.99 (s, 2F).

HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₁₈H₁₅F₂N₃O: 350.1081, found: 350.1080.

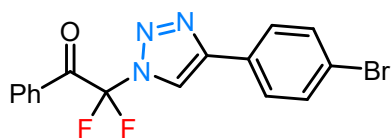


4ab

2-(4-(3,5-Dimethoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2,2-difluoro-1-phenylethan-1-one (4ab)

White solid (60%), m.p. = 75.4 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃) δ 8.30 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.02 (s, 2H), 6.47 (s, 1H), 3.79 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 181.72 (t, ²*J*_{C-F} = 29.0 Hz), 161.35, 148.62, 135.40, 130.86, 130.69, 130.35, 129.07, 117.75, 111.75 (t, ¹*J*_{C-F} = 268.0 Hz), 104.15, 101.48, 55.49. ¹⁹F NMR (376 MHz, CDCl₃) δ -82.30 (s, 2F). HRMS (ESI) *m/z* calcd [M + H]⁺ = for C₁₈H₁₅F₂N₃O₃: 360.1160, found: 360.1157.

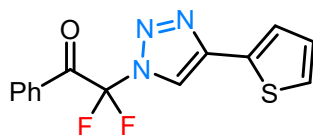


4ac

2-(4-(4-Bromophenyl)-1H-1,2,3-triazol-1-yl)-2,2-difluoro-1-phenylethan-1-one (4ac)

White solid (64%) , m.p. = 152.2 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃) δ 8.28 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 181.75 (t, ²*J*_{C-F} = 29.5 Hz), 147.71, 135.45, 132.32, 130.90, 130.46, 129.11, 127.97, 127.69, 123.32, 117.45, 111.80 (t, ¹*J*_{C-F} = 268.5 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -82.32 (s, 2F). HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₁₆H₁₀BrF₂N₃O: 399.9873, found: 399.9876.

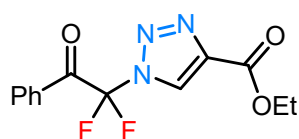


4ad

2,2-Difluoro-1-phenyl-2-(4-(thiophen-2-yl)-1H-1,2,3-triazol-1-yl)ethan-1-one (4ad)

White solid (48%) , m.p. = 101.8 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 8.01 (d, *J* = 4.0 Hz, 2H), 7.81 (s, 1H), 7.66 (t, *J* = 6.0 Hz, 1H), 7.51-7.43 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 181.74 (t, ²*J*_{C-F} = 29.0 Hz), 144.87, 135.41, 130.91, 130.44, 130.12, 129.09, 127.00, 125.78, 122.91, 116.98, 111.72 (t, ¹*J*_{C-F} = 268.0 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -82.26 (s, 2F). HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₁₄H₉F₂N₃OS: 328.0327, found: 328.0329.

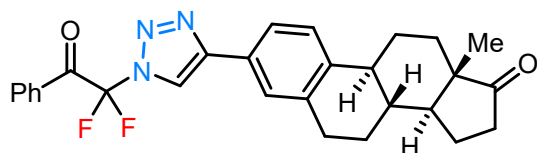


4ae

Ethyl 1-(1,1-difluoro-2-oxo-2-phenylethyl)-1H-1,2,3-triazole-4-carboxylate (4ae)

Yellow oil (59%), purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃) δ 8.59 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 6.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 4.41 (q, *J* = 6.7 Hz, 2H), 1.36 (t, *J* = 6.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 181.26 (t, ²*J*_{C-F} = 30.0 Hz), 159.65, 140.90, 135.73, 130.34 (t, ³*J*_{C-F} = 2.5 Hz), 129.20, 128.07, 126.21, 111.98 (t, ¹*J*_{C-F} = 272.0 Hz), 61.93, 14.22. ¹⁹F NMR (376 MHz, CDCl₃) δ -82.74 (s, 2F). HRMS (ESI) *m/z* calcd [M + H]⁺ = for C₁₃H₁₁F₂N₃O₃: 296.0847, found: 296.0843.

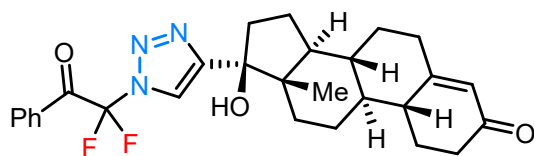


4af

4-(1-(1,1-Difluoro-2-oxo-2-phenylethyl)-1H-1,2,3-triazol-4-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4af)

White solid (70%) , m.p. = 144.5 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.69-7.62 (m, 3H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 2.99-2.96 (m, 2H), 2.55-2.43 (m, 2H), 2.36-2.31 (m, 1H), 2.20-1.96 (m, 4H), 1.68-1.45 (m, 6H), 0.93 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 220.92, 181.81 (t, ²*J*_{C-F} = 29.0 Hz), 148.76, 141.09, 137.42, 135.38, 130.97, 130.45, 129.07, 126.72, 126.44, 126.14, 123.56, 117.03, 111.74 (t, ¹*J*_{C-F} = 267.5 Hz), 50.55, 48.04, 44.51, 38.08, 35.92, 31.62, 29.42, 26.45, 25.75, 21.66, 13.92. ¹⁹F NMR (376 MHz, CDCl₃) δ -82.24 (s, 2F). HRMS (ESI) *m/z* calcd [M + CH₃OH + H]⁺ = for C₂₈H₂₇F₂N₃O₂: 508.2406, found: 508.2404.

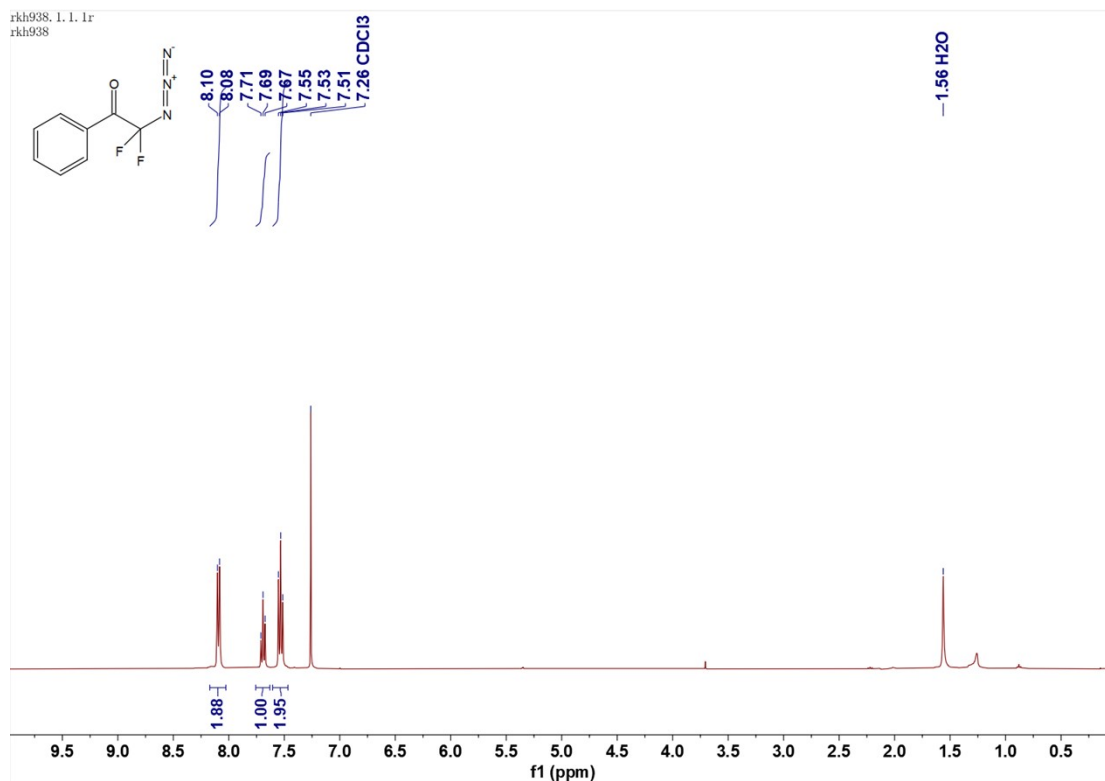


4ag

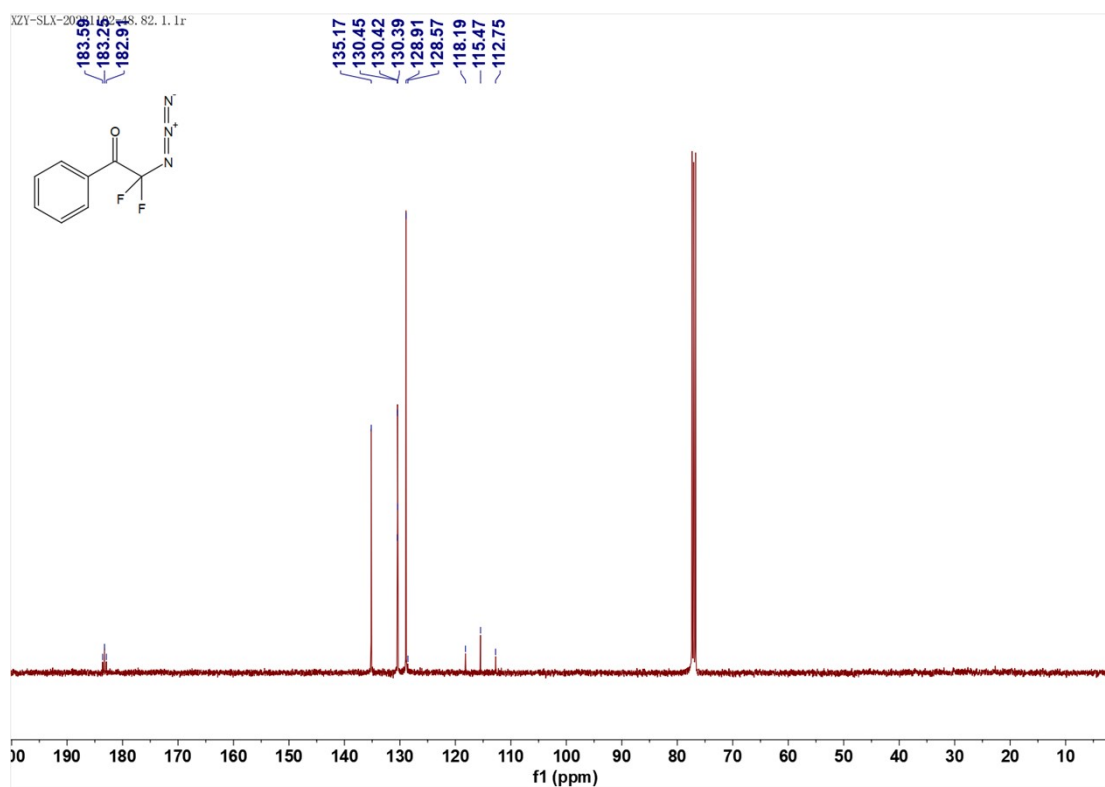
17-(1-(1,1-Difluoro-2-oxo-2-phenylethyl)-1H-1,2,3-triazol-4-yl)-17-hydroxy-13-methyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (4ag)

White solid (41%) , m.p. = 95.3 °C, purified by silica-gel column chromatography (PE/EA).

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 12.0 Hz, 3H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 5.77 (s, 1H), 3.71-3.49 (m, 1H), 2.46-2.30 (m, 3H), 2.28-2.15 (m, 3H), 2.12-2.01 (m, 2H), 1.90-1.82 (m, 2H), 1.73-1.69 (m, 1H), 1.54-1.35 (m, 5H), 1.24-1.18 (m, 1H), 1.06 (s, 3H), 0.89 (t, *J* = 6.0 Hz, 1H), 0.65 (qd, *J* = 10.6, 4.0 Hz, 1H), 0.45 (td, *J* = 16.0, 4.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 200.17, 181.91 (t, ²*J*_{C-F} = 30.0 Hz), 166.94, 154.94, 135.34, 130.95, 130.40, 129.02, 124.54, 119.54, 111.78 (t, ¹*J*_{C-F} = 268.0 Hz), 82.38, 48.80, 48.21, 47.31, 42.52, 41.11, 38.06, 36.46, 35.51, 32.63, 30.67, 26.49, 26.07, 23.69, 14.26. ¹⁹F NMR (376 MHz, CDCl₃) δ -82.35 (s, 2F). HRMS (ESI) *m/z* calcd [M + Na]⁺ = for C₂₈H₃₁F₂N₃O₃: 518.2231, found: 518.2229.

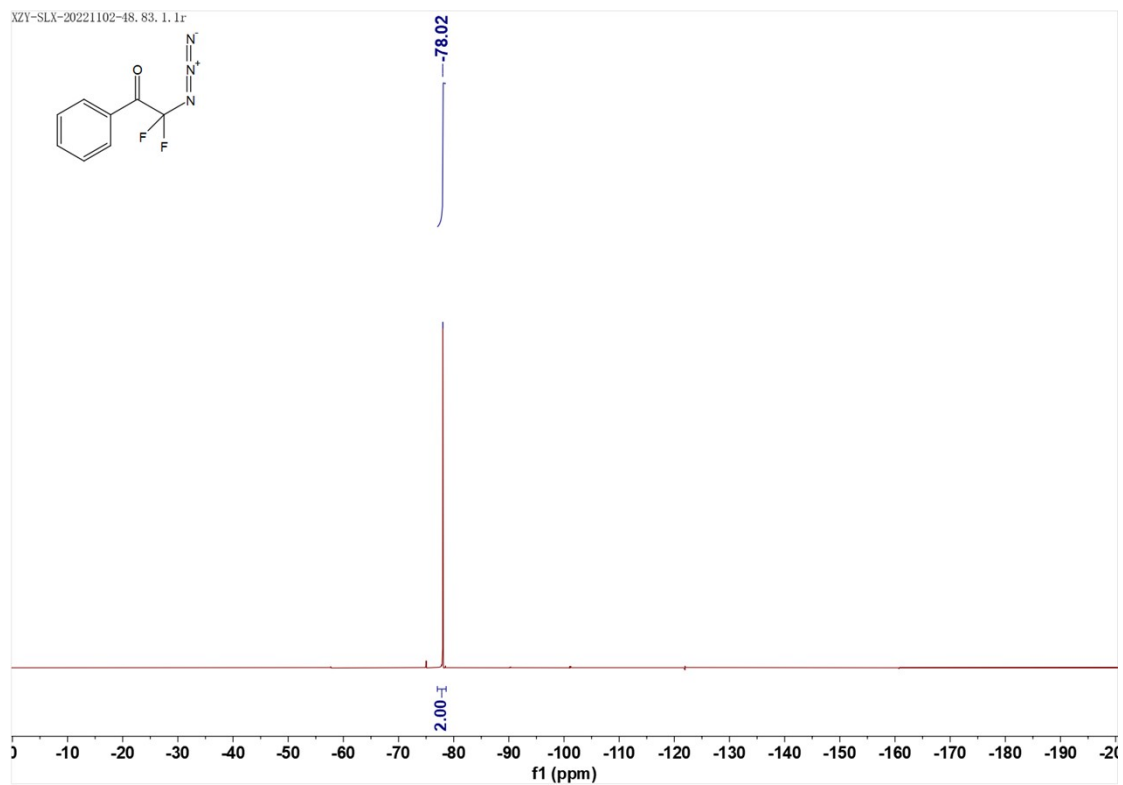


¹H NMR spectra of 2a



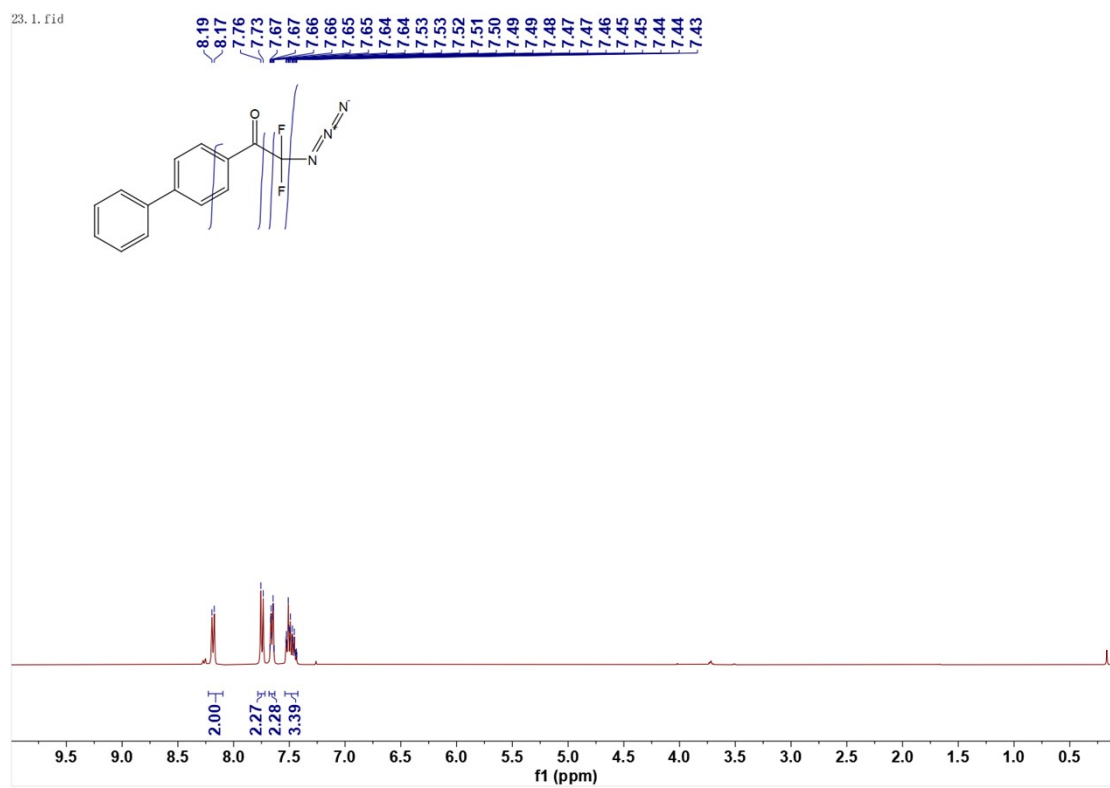
¹³C NMR spectra of 2a

XZY-SLX-20221102-48.83.1.f

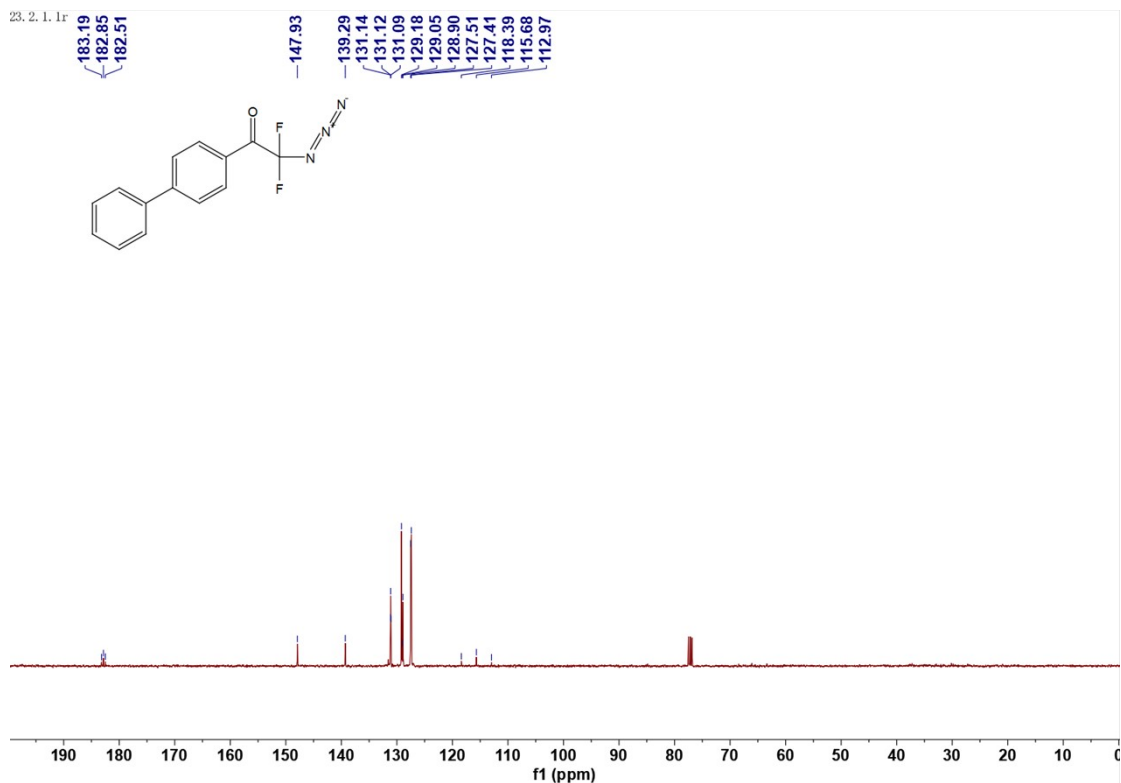


¹⁹F NMR spectra of 2a

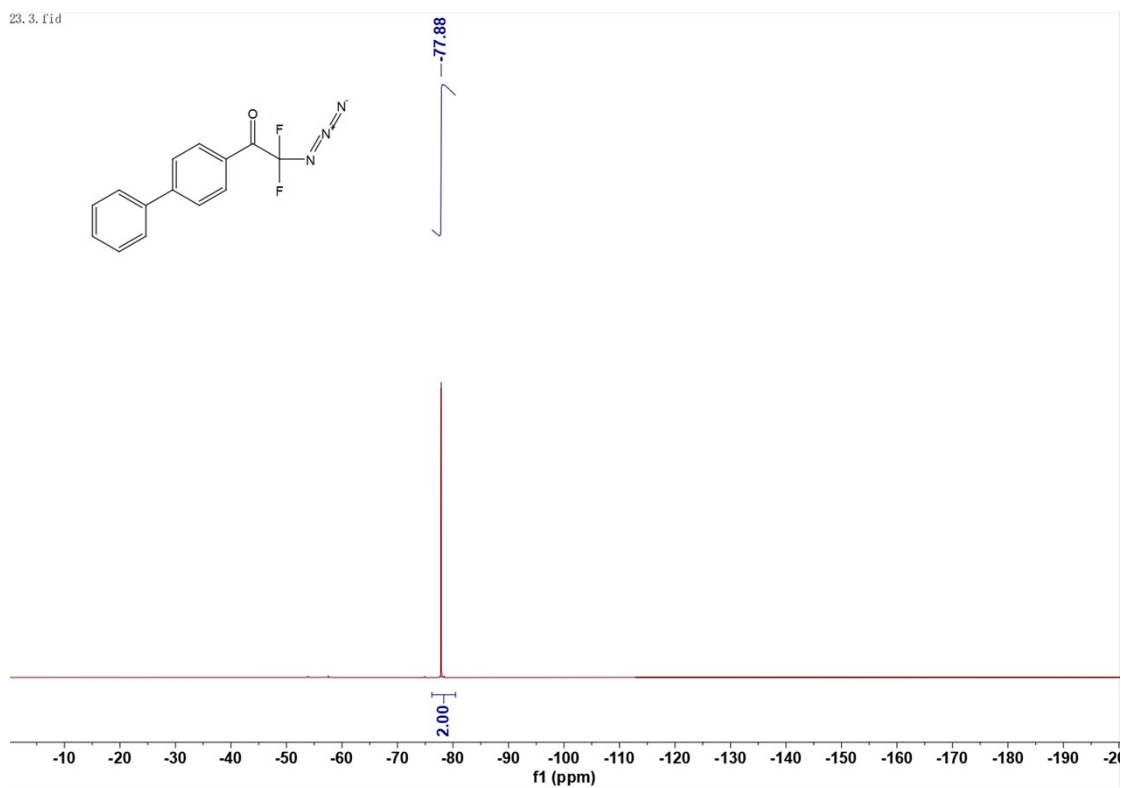
23.1.fid



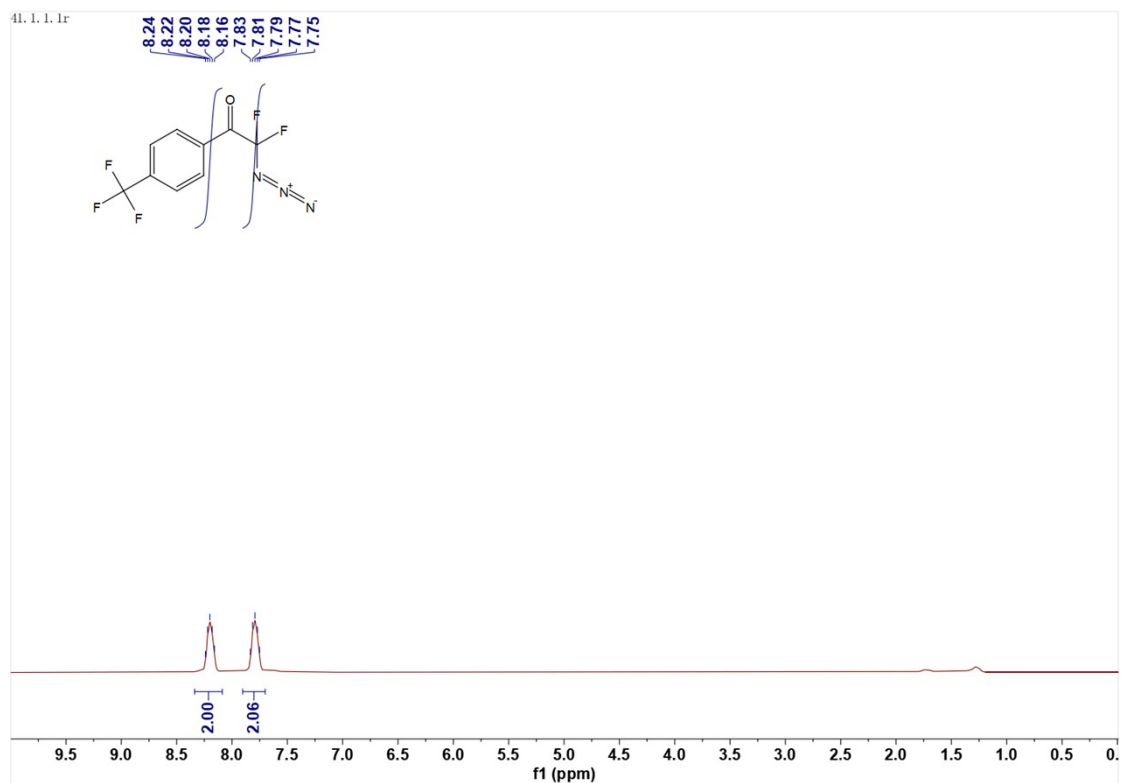
¹H NMR spectra of 2b



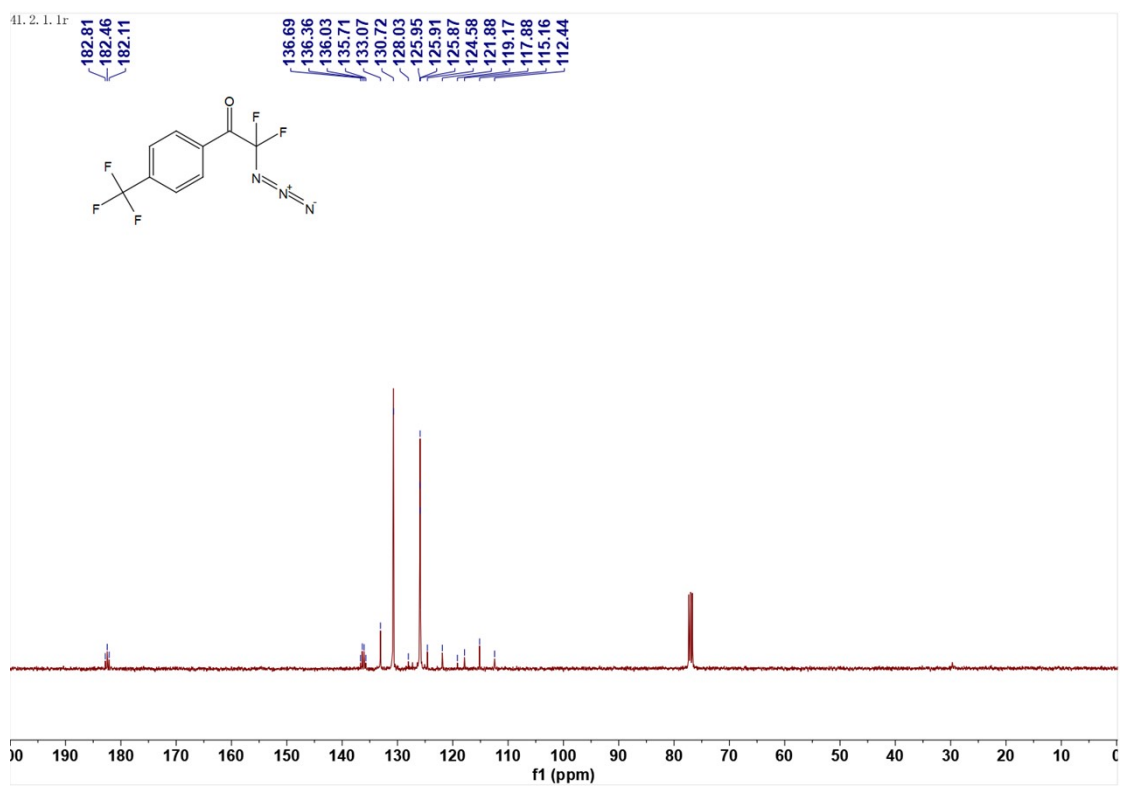
¹³C NMR spectra of 2b



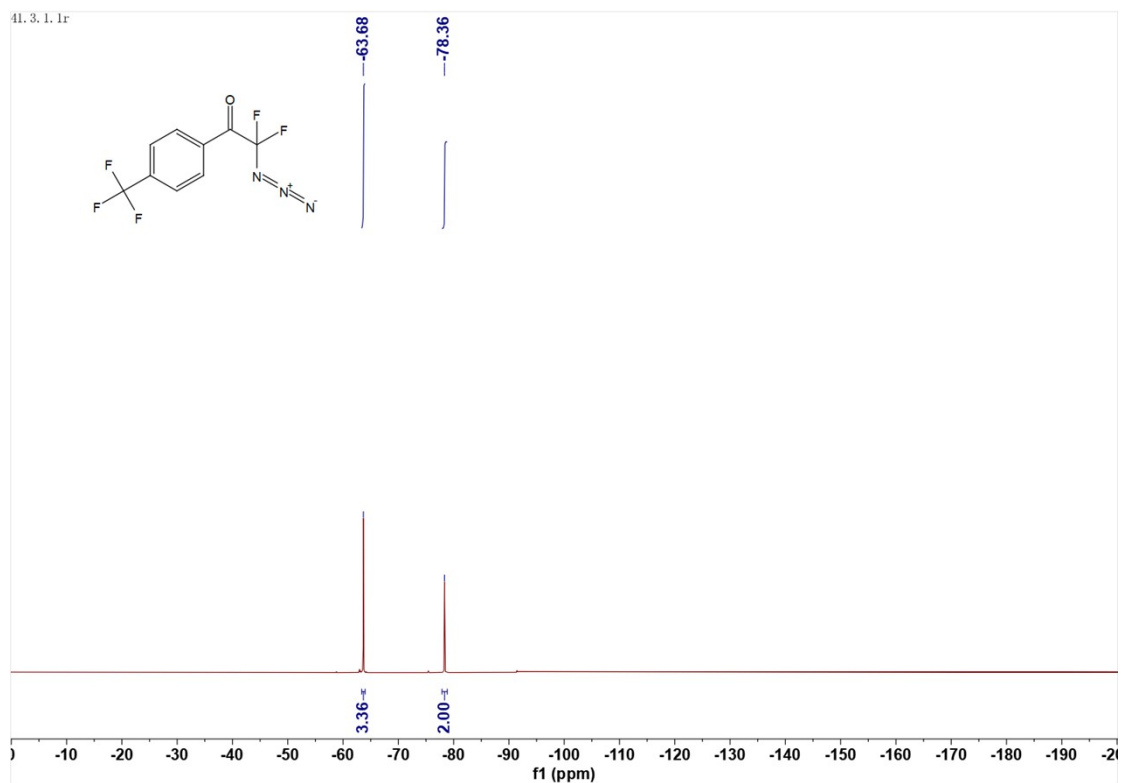
¹⁹F NMR spectra of 2b



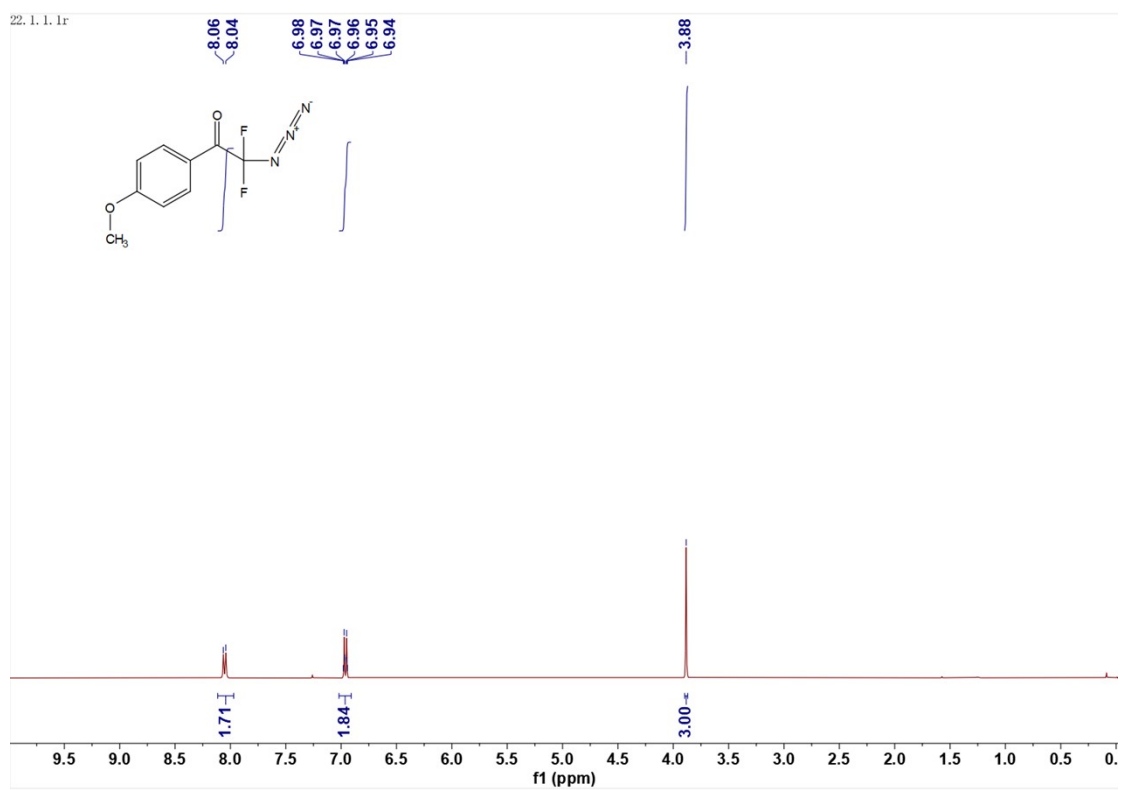
¹H NMR spectra of 2c



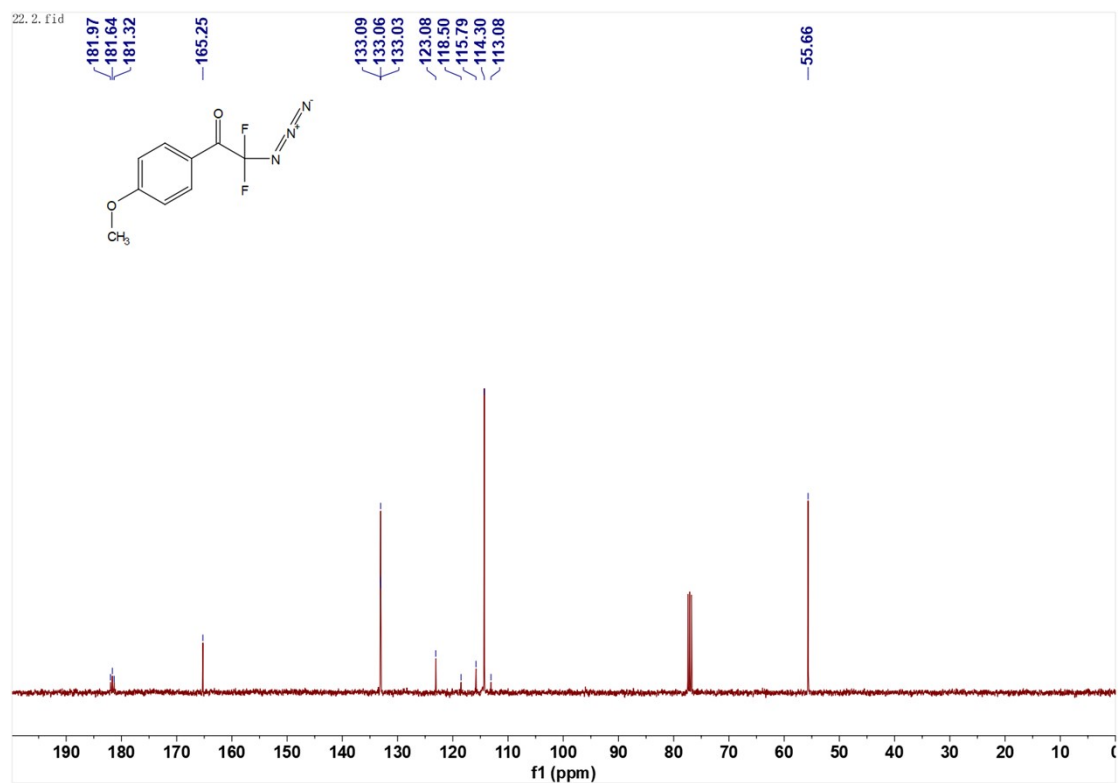
¹³C NMR spectra of 2c



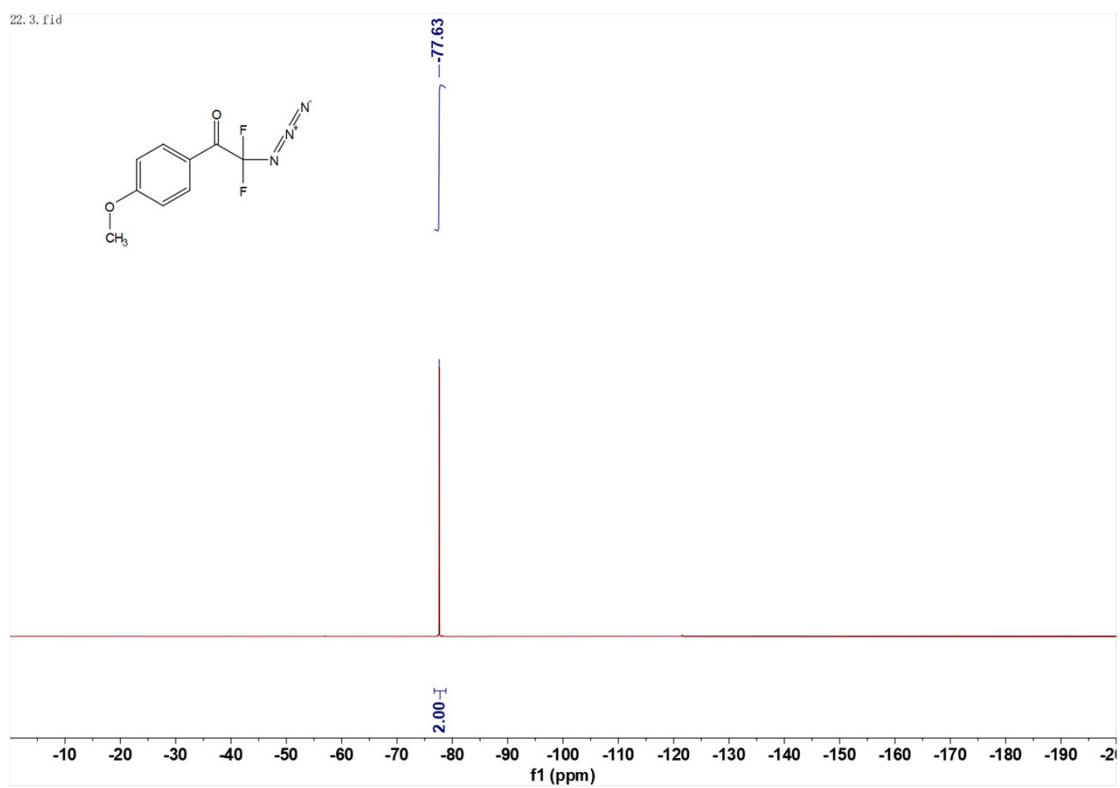
¹⁹F NMR spectra of 2c



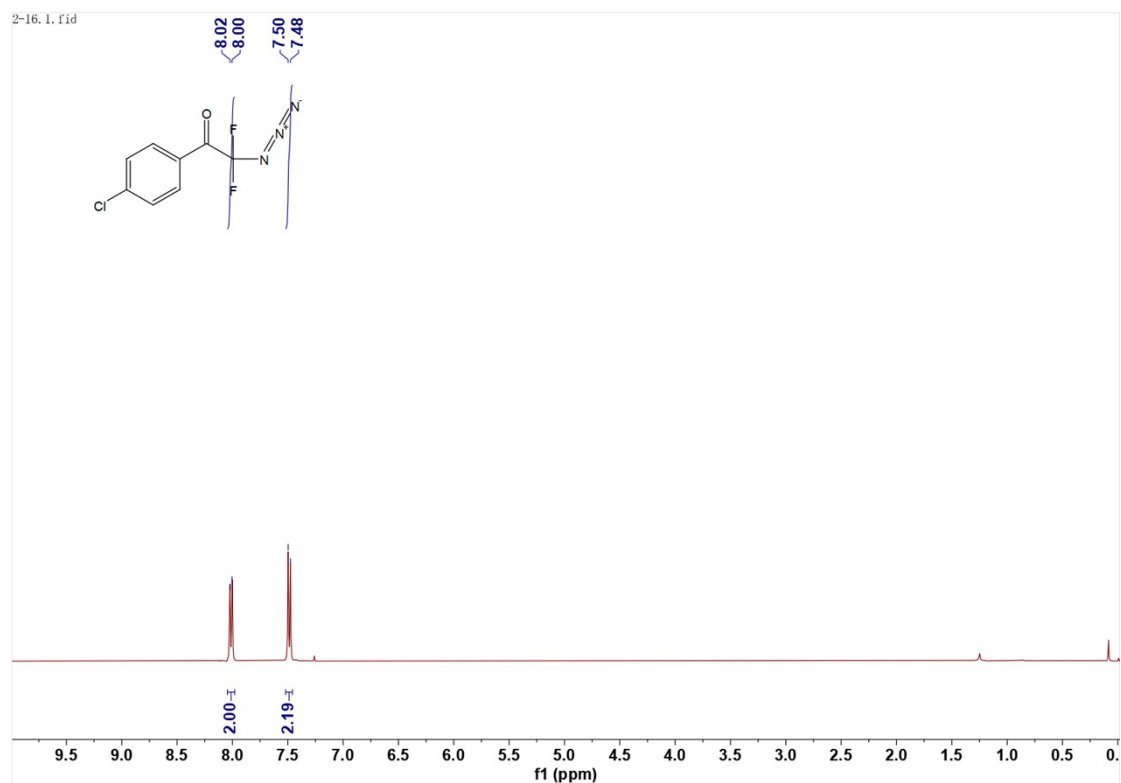
¹H NMR spectra of 2d



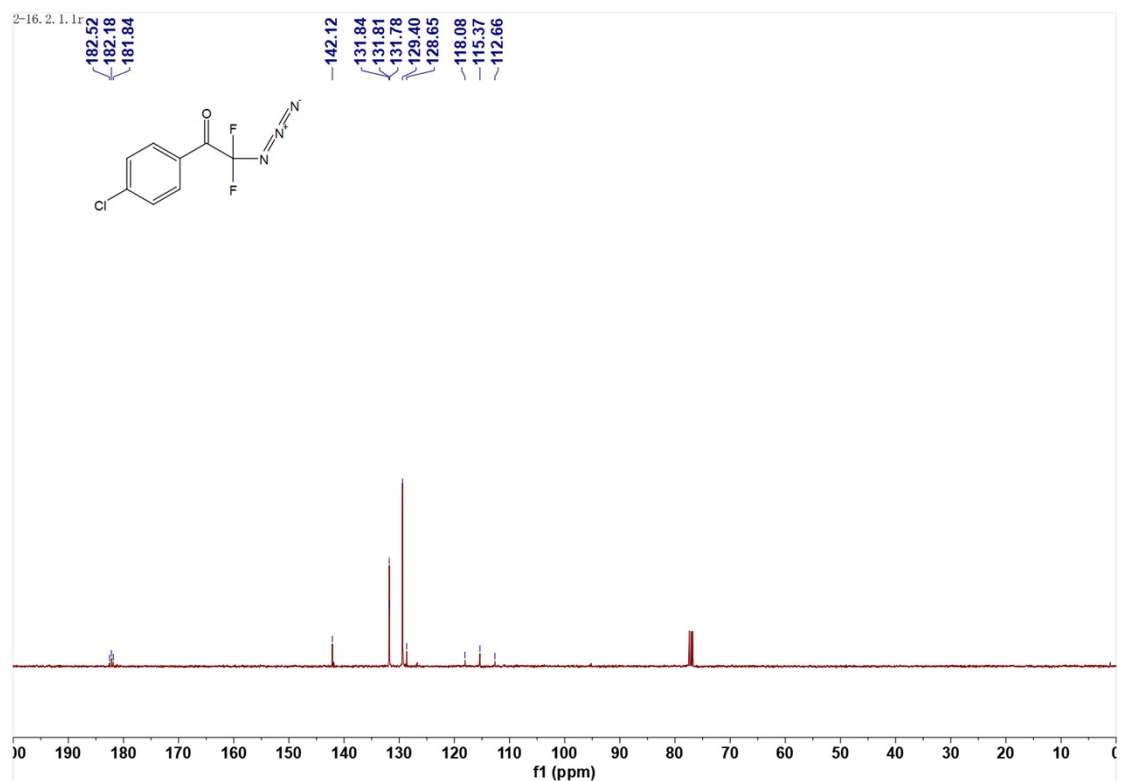
¹³C NMR spectra of 2d



¹⁹F NMR spectra of 2d

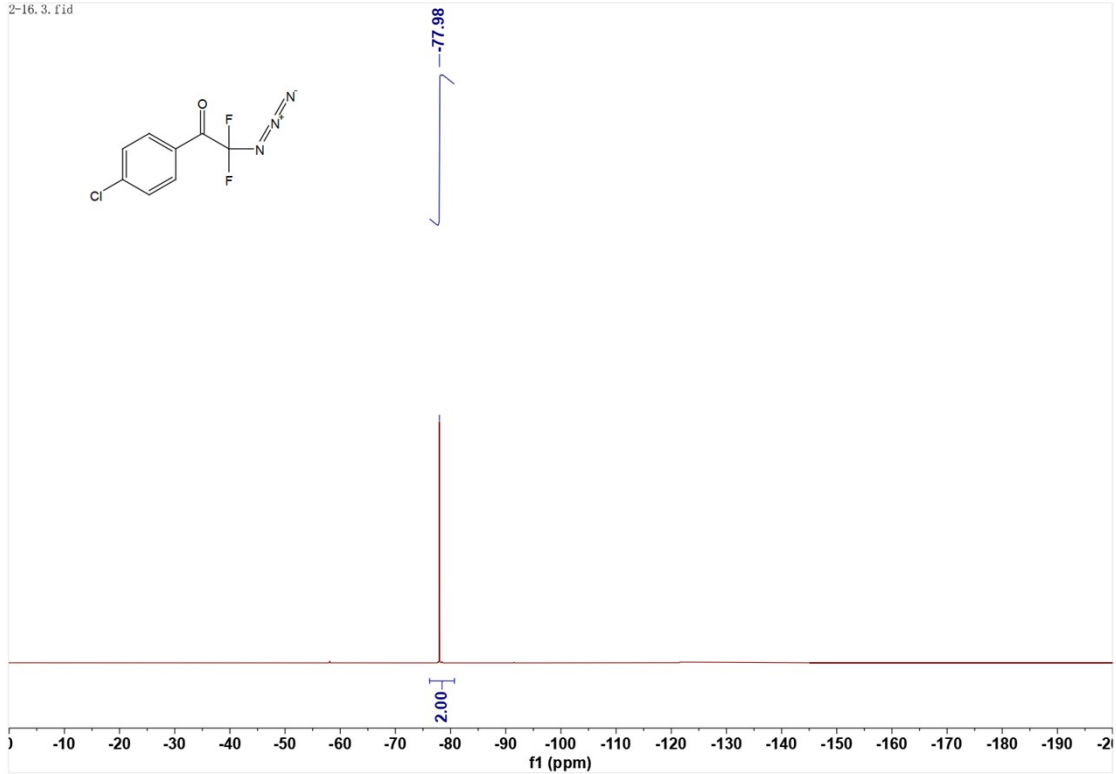


¹H NMR spectra of 2e



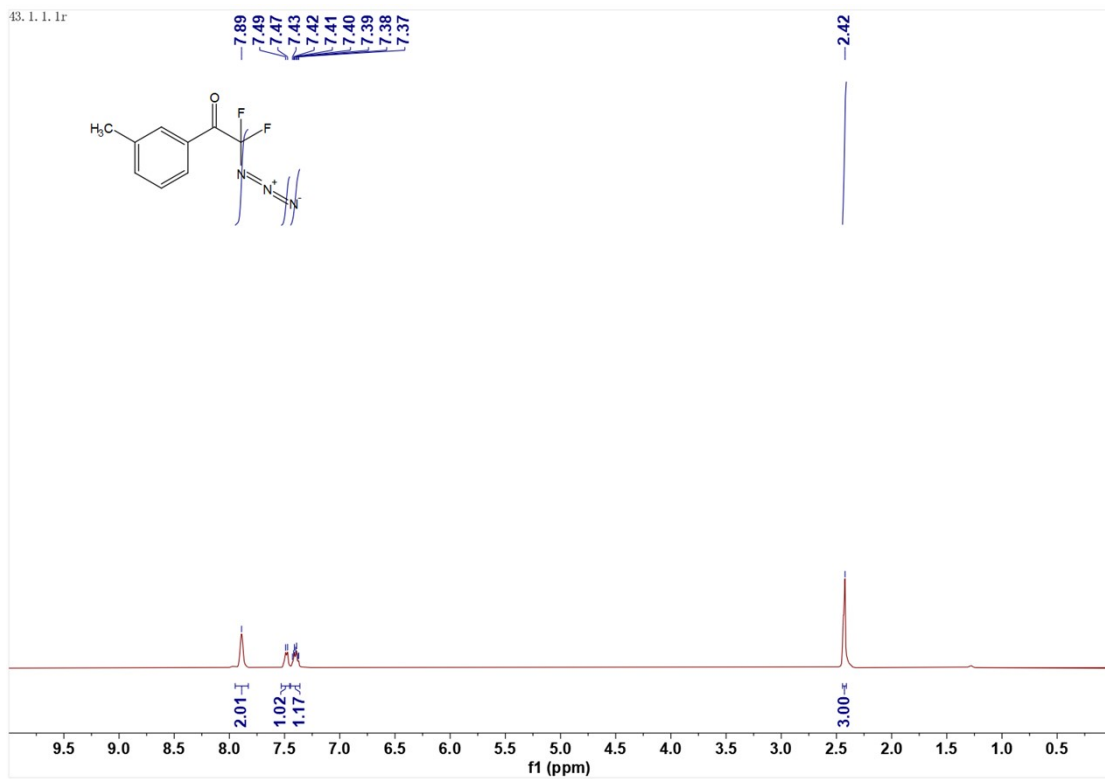
¹³C NMR spectra of 2e

2-16. 3. fid

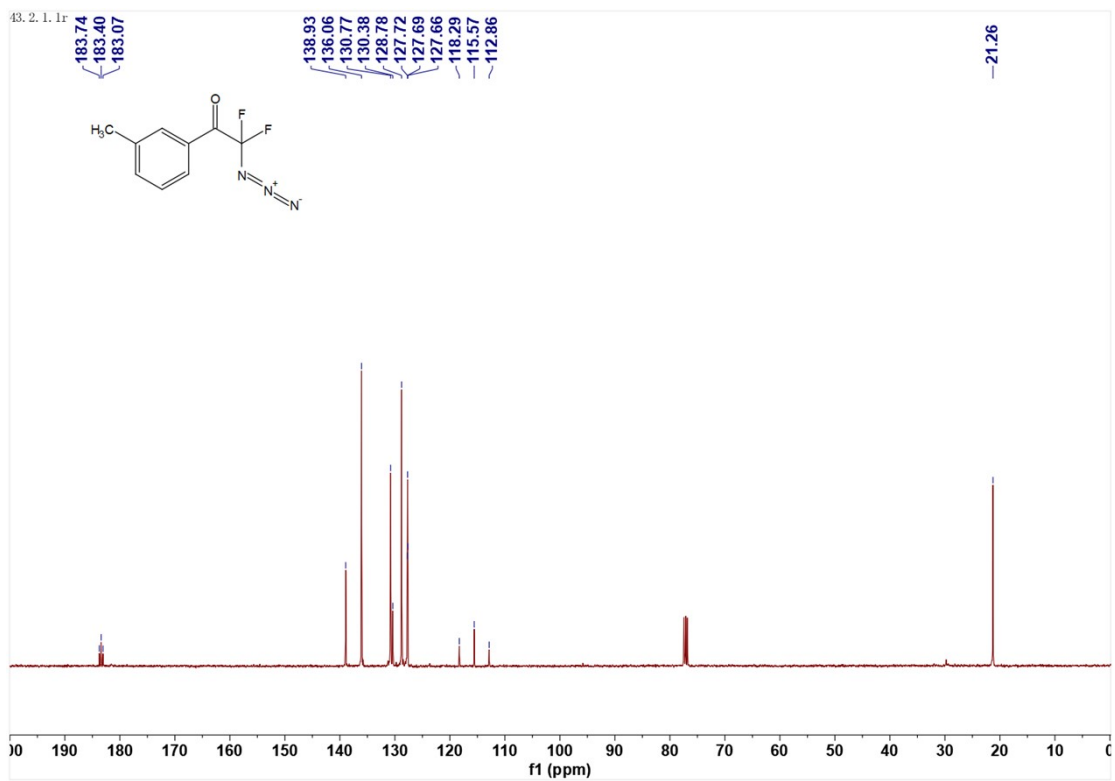


^{19}F NMR spectra of 2e

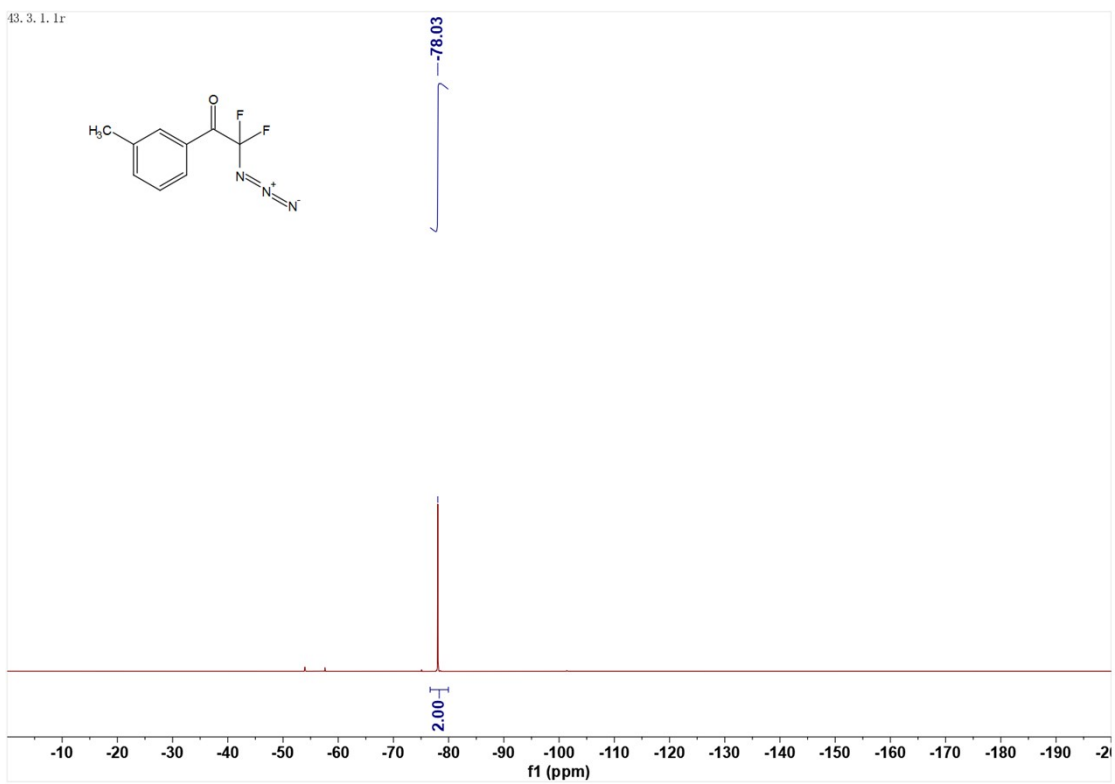
43. 1. 1. 1r



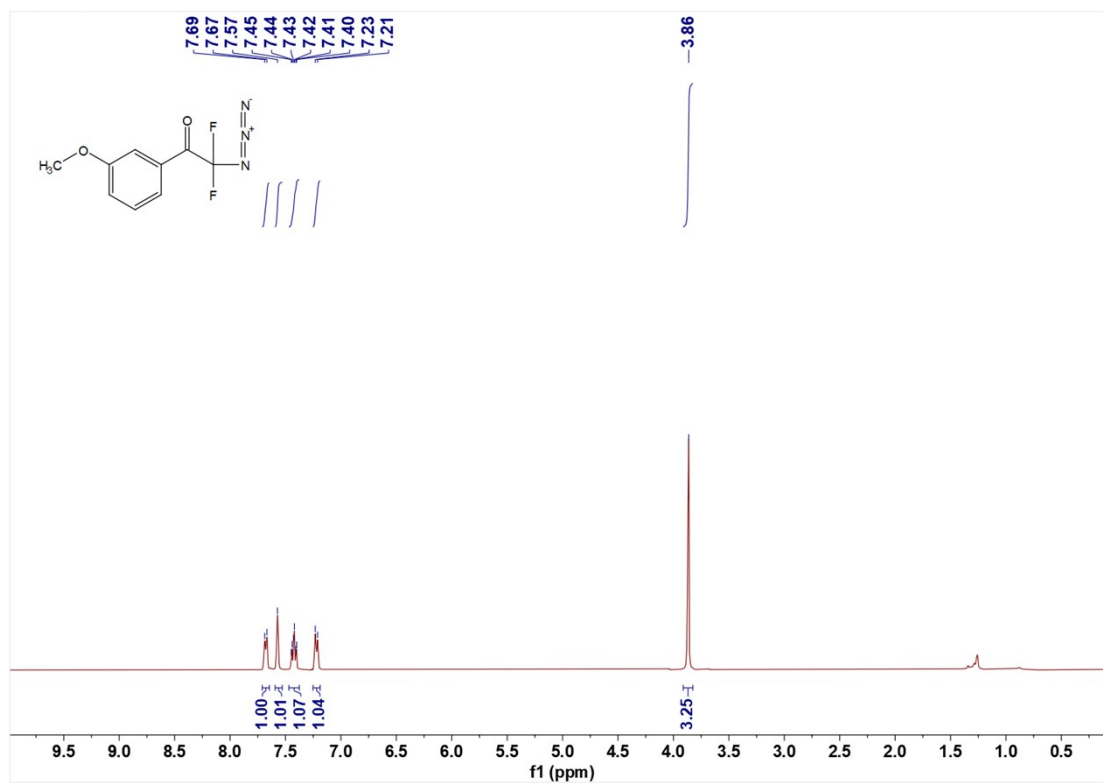
^1H NMR spectra of 2f



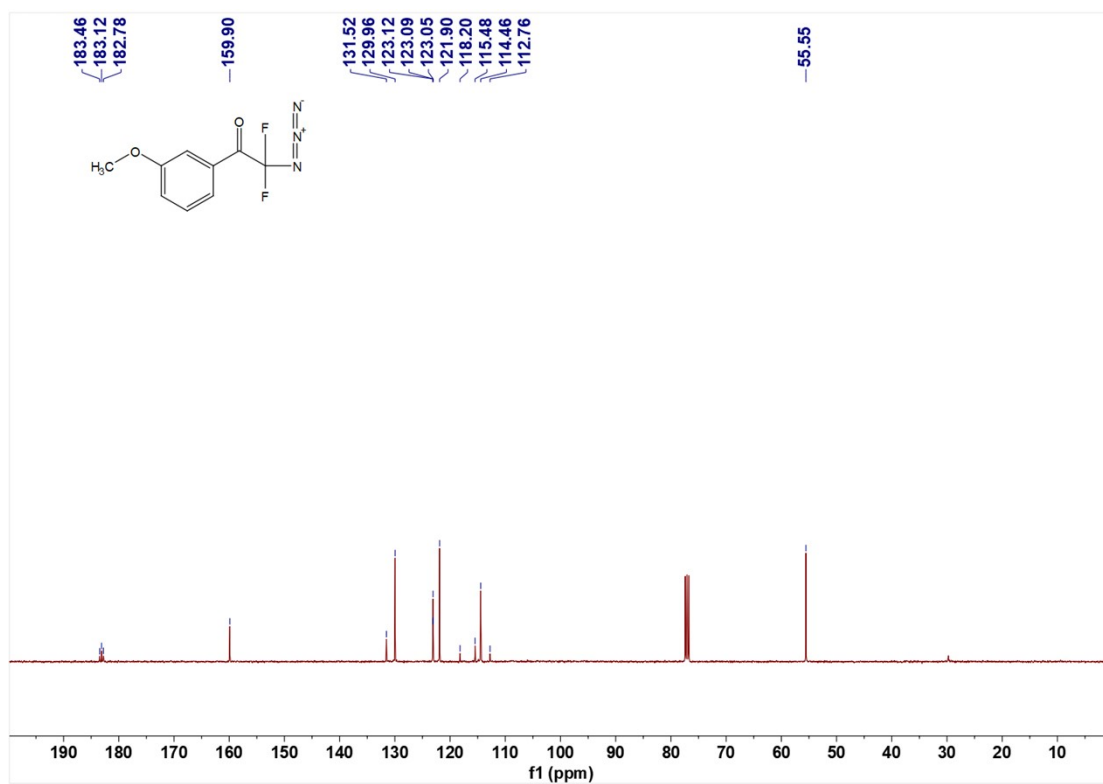
¹³C NMR spectra of 2f



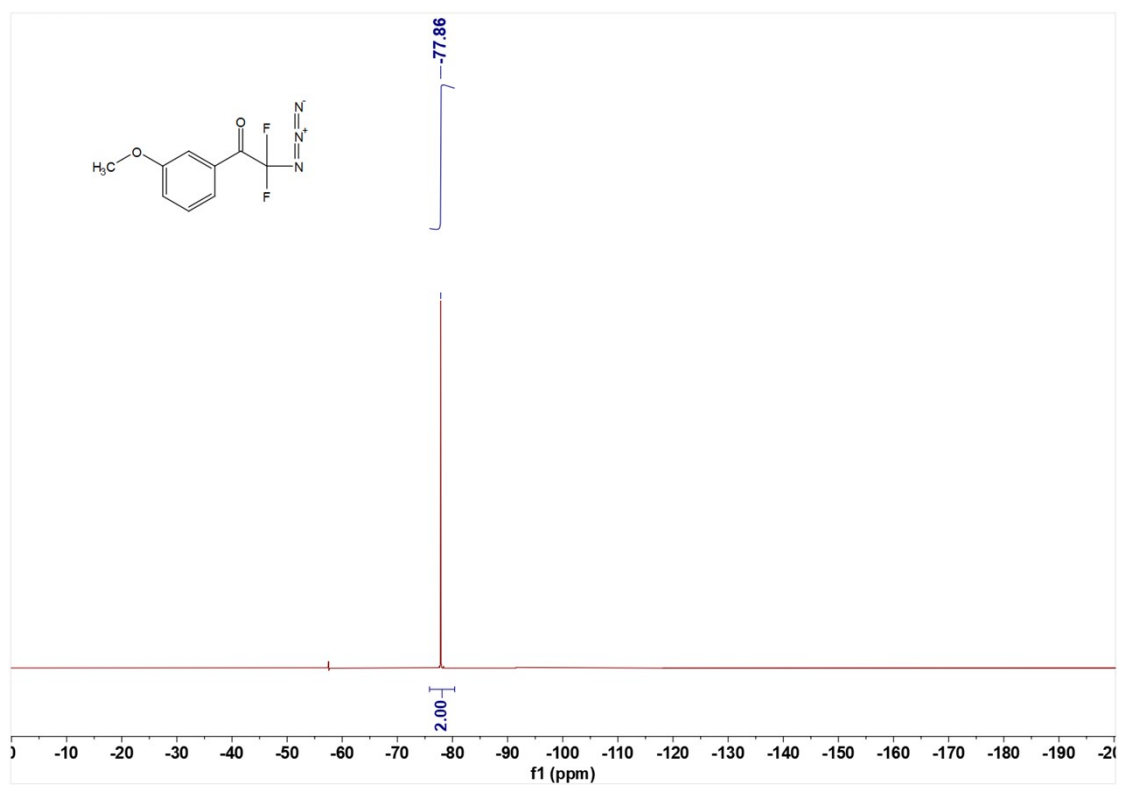
¹⁹F NMR spectra of 2f



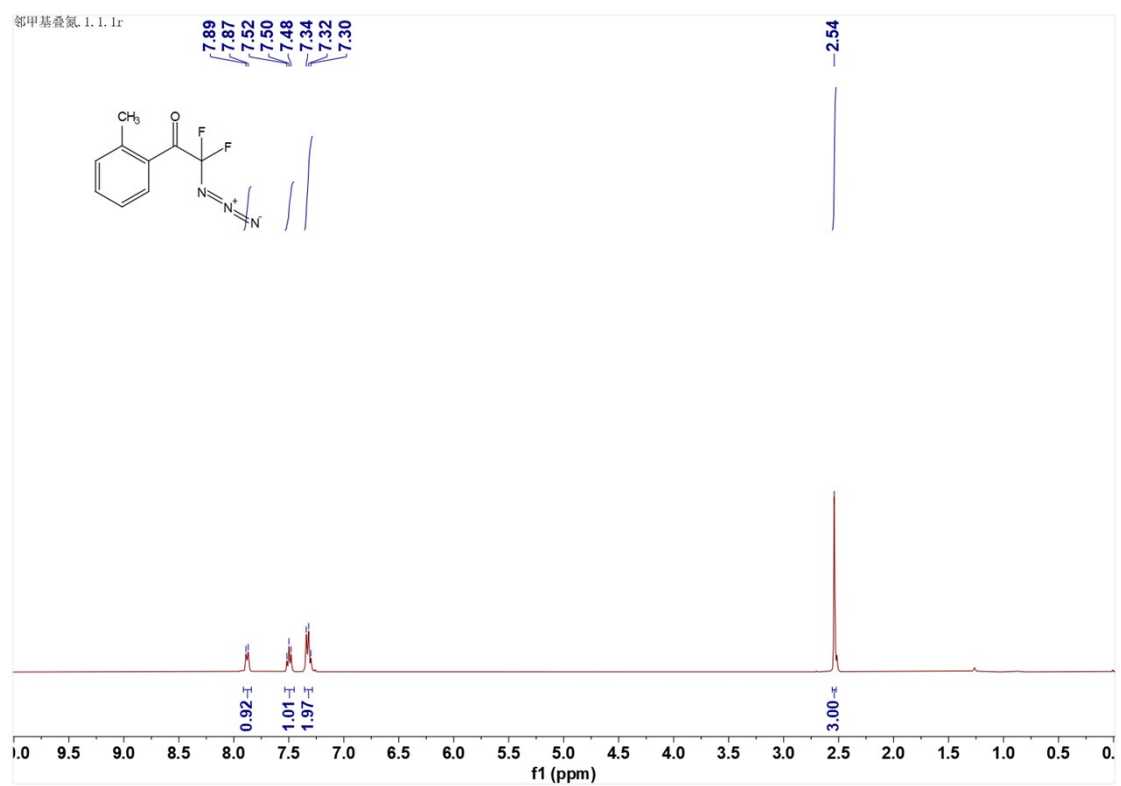
¹H NMR spectra of 2g



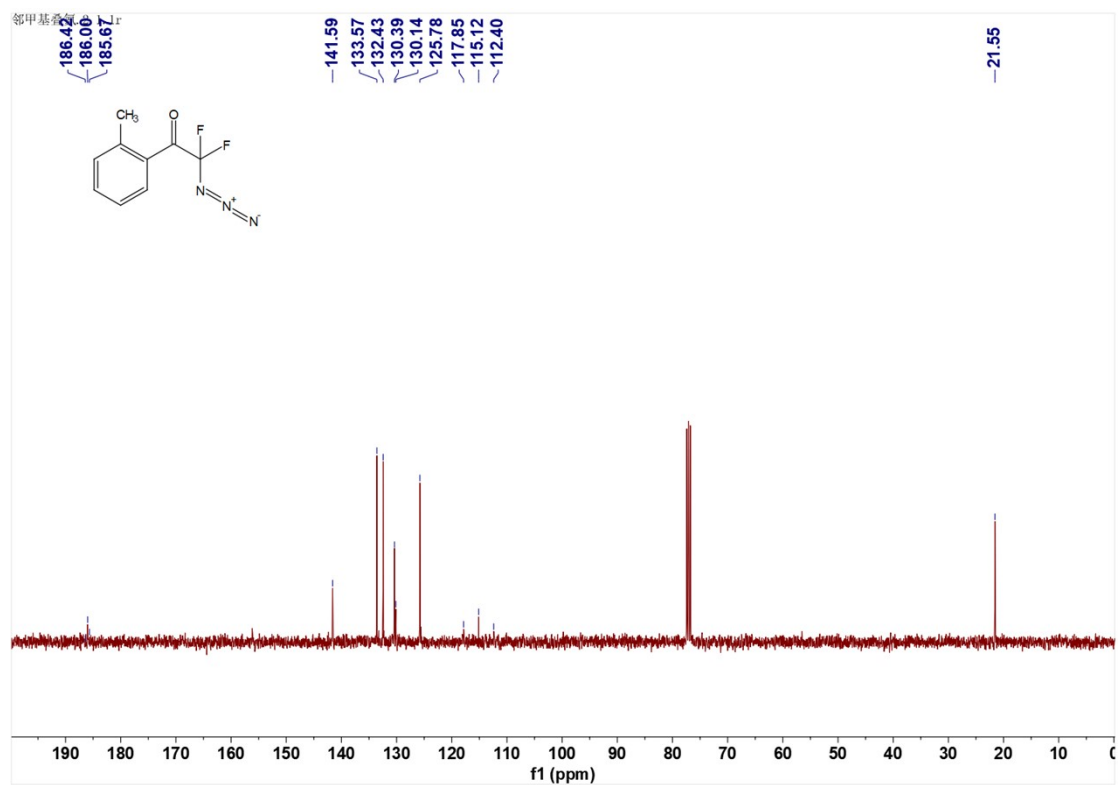
¹³C NMR spectra of 2g



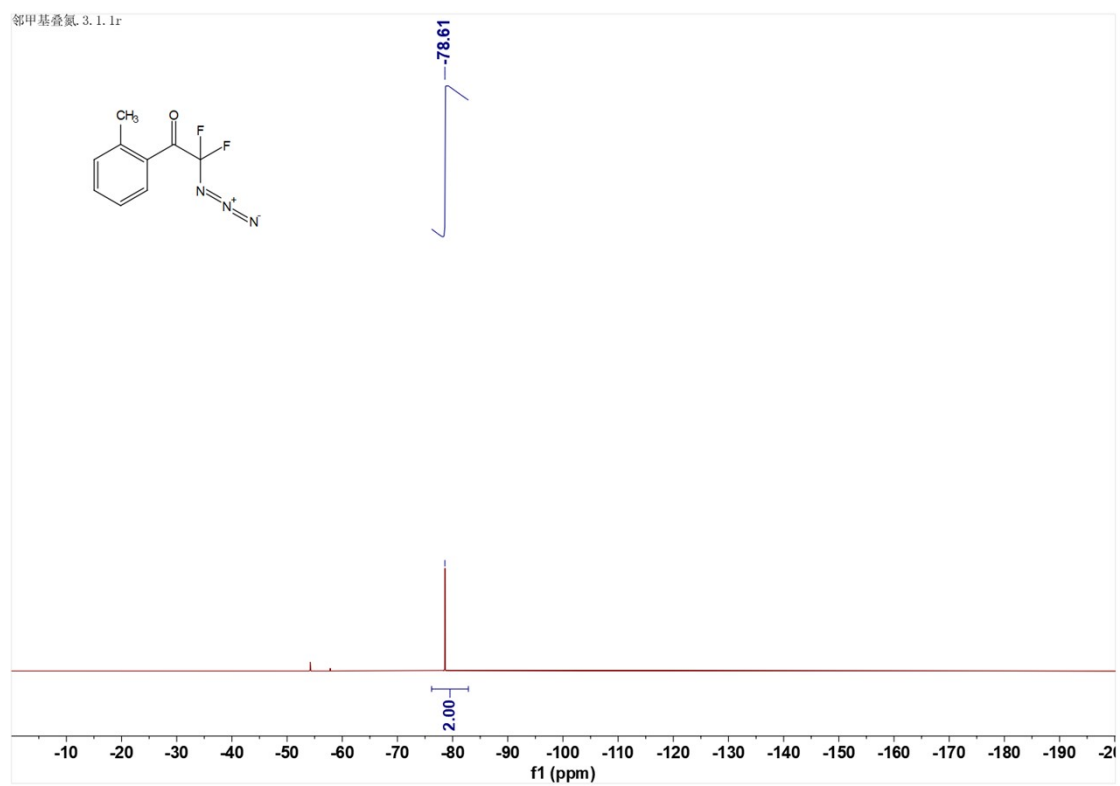
^{19}F NMR spectra of 2g



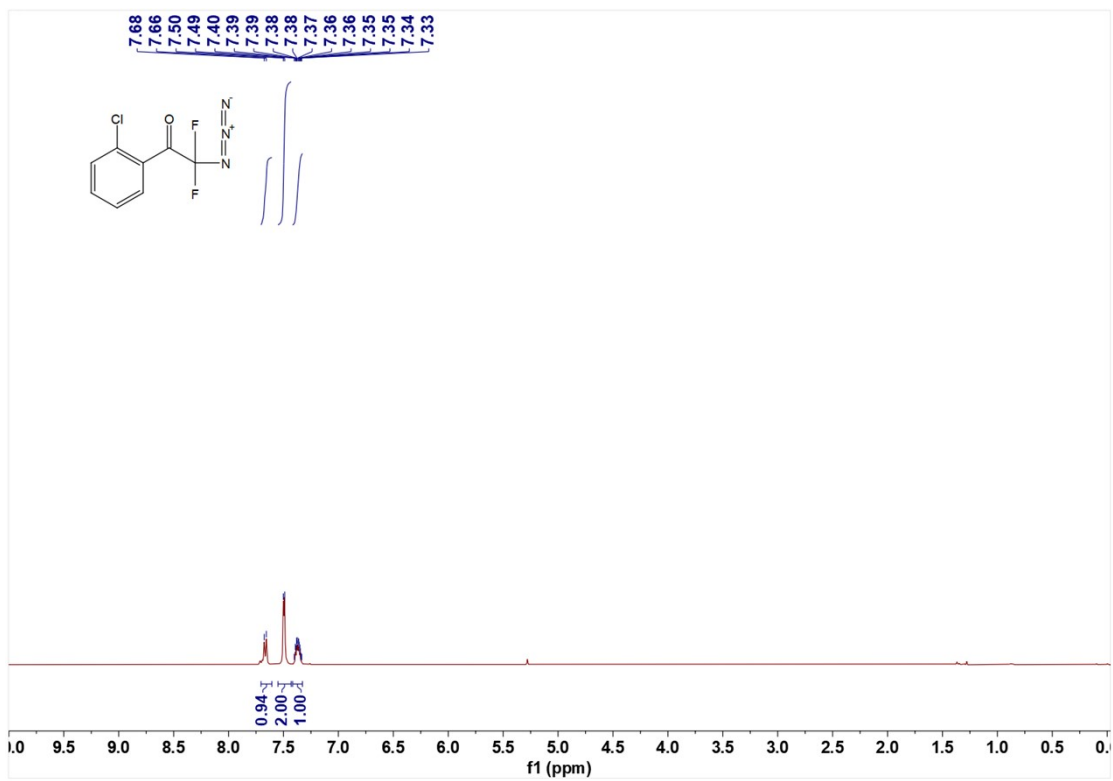
^1H NMR spectra of 2h



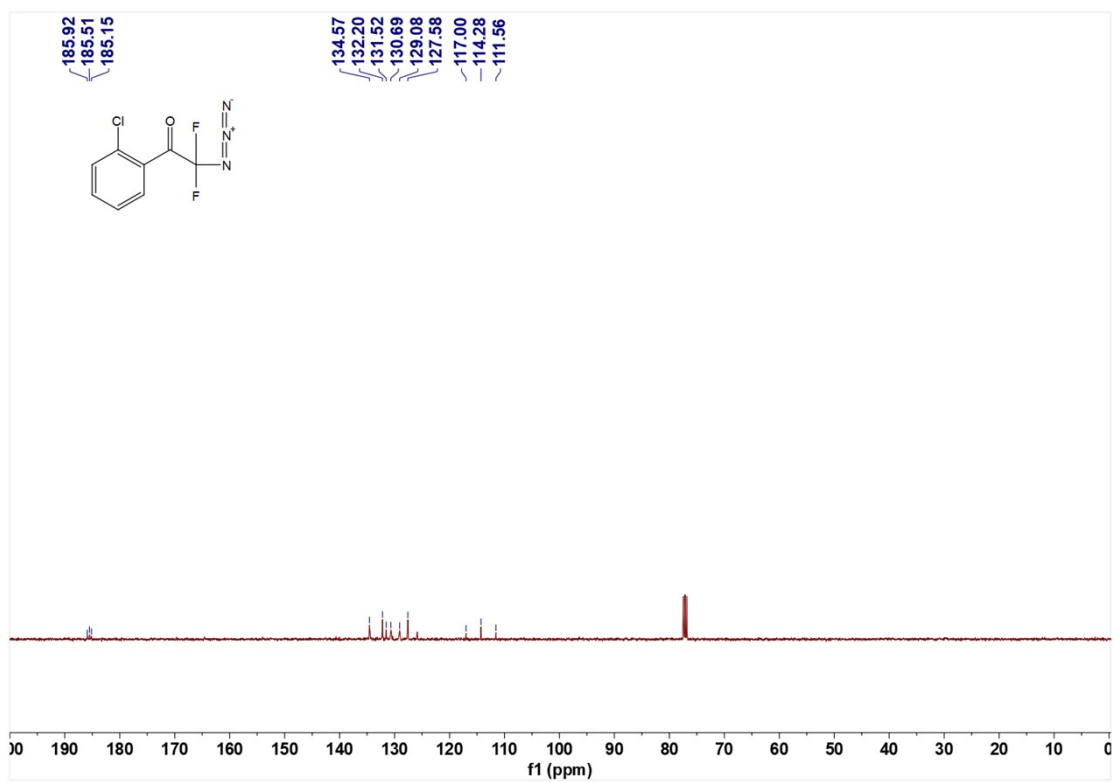
¹³C NMR spectra of 2h



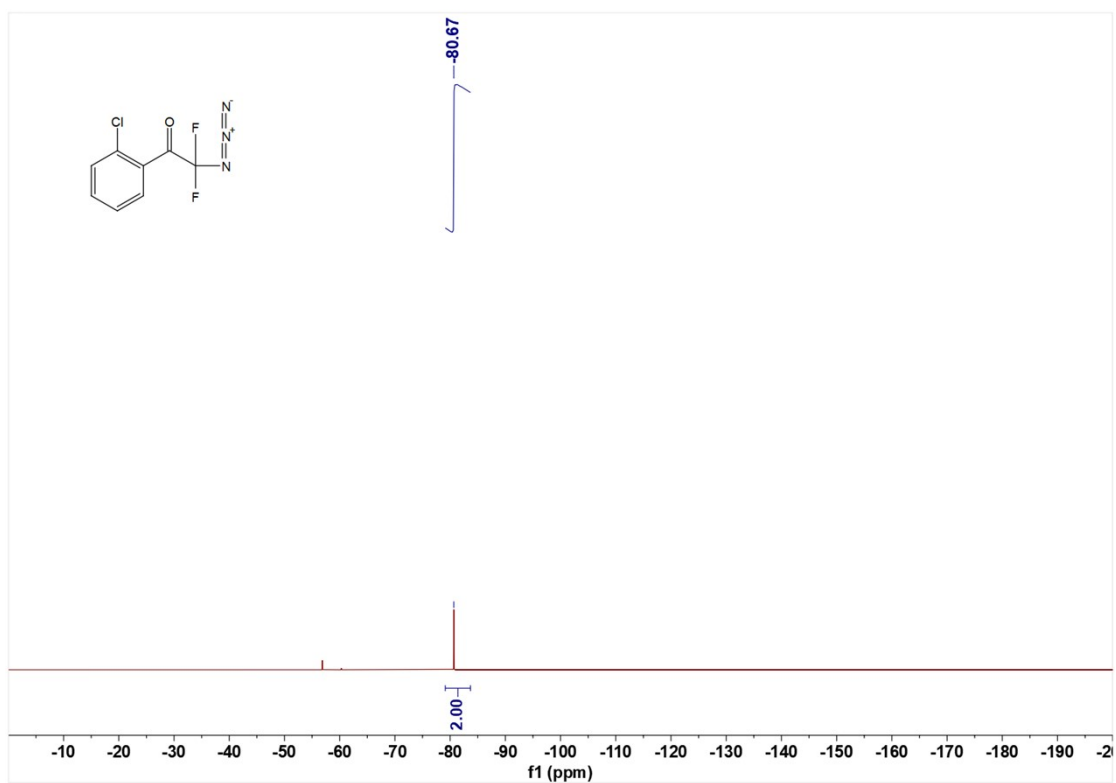
¹⁹F NMR spectra of 2h



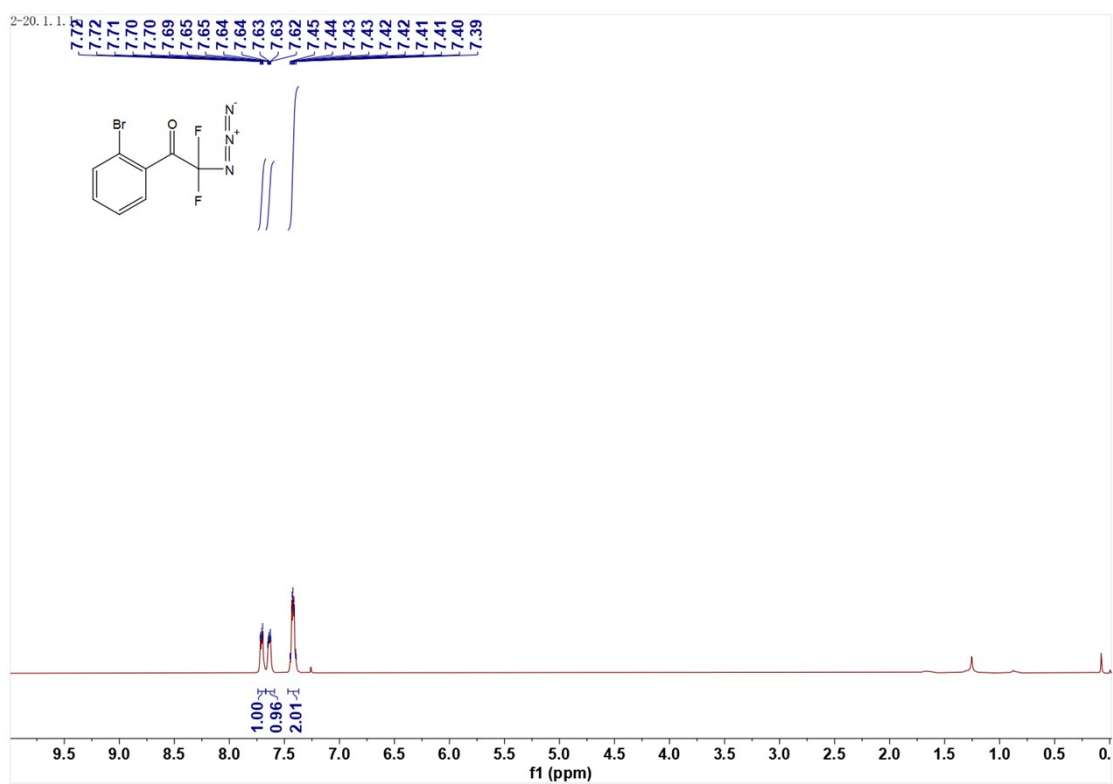
¹H NMR spectra of 2i



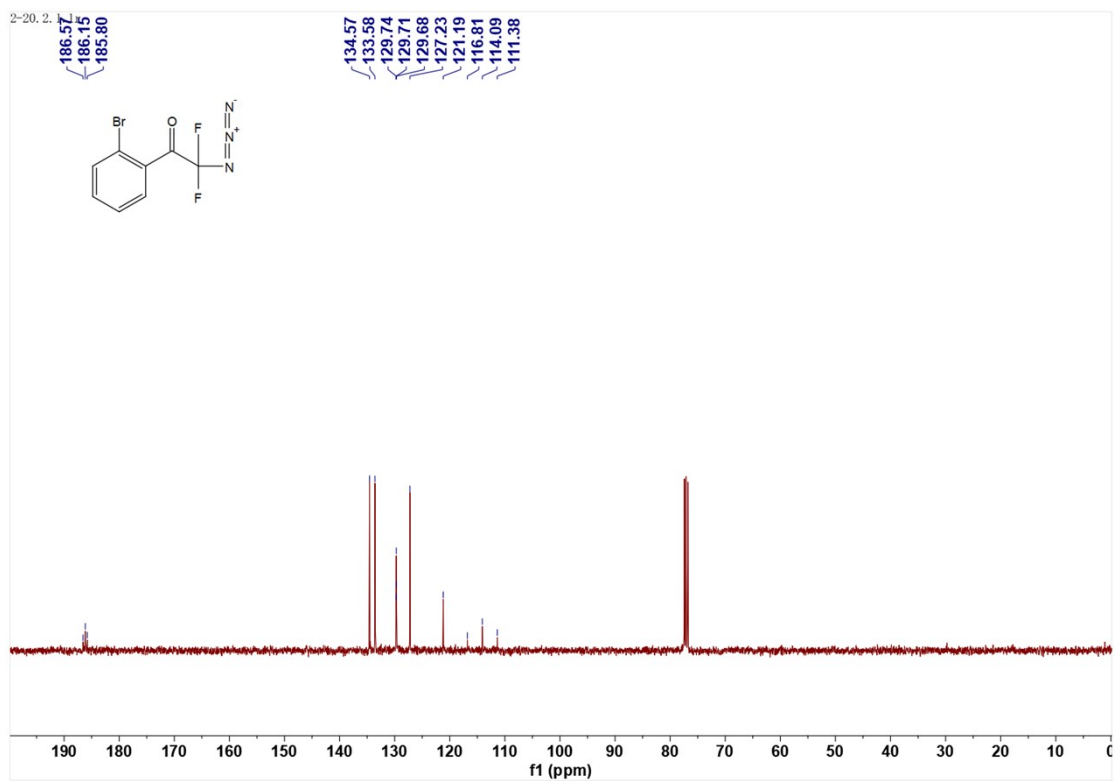
¹³C NMR spectra of 2i



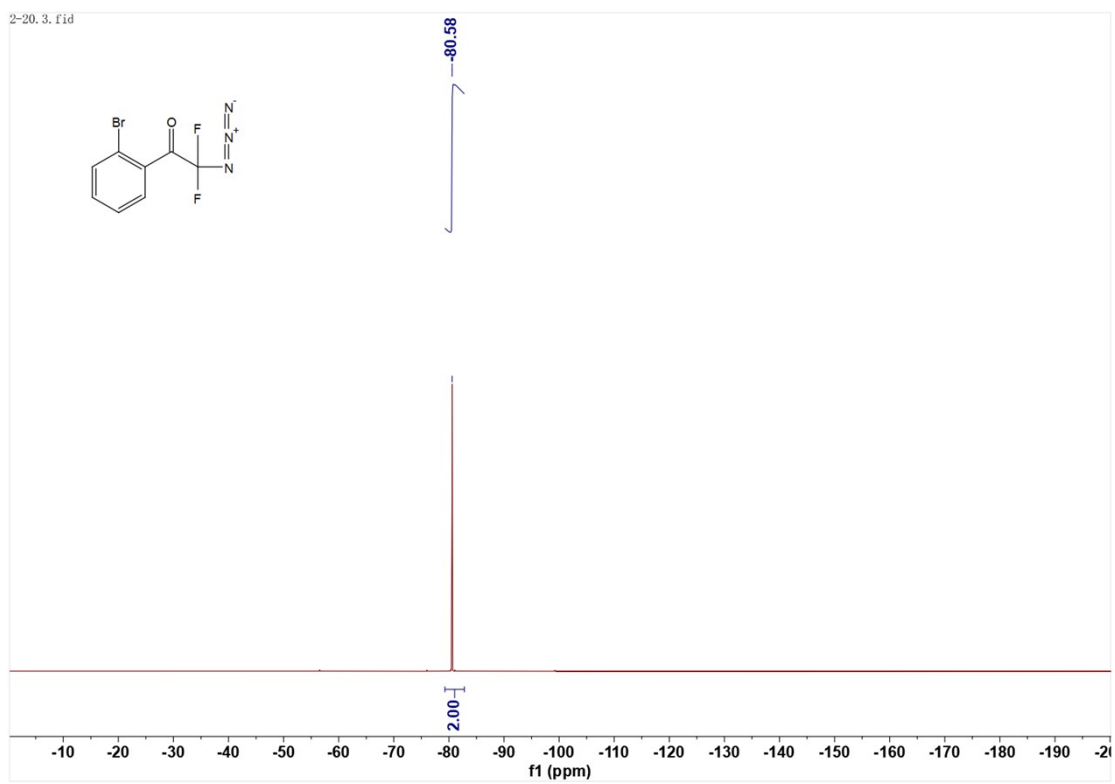
^{19}F NMR spectra of 2i



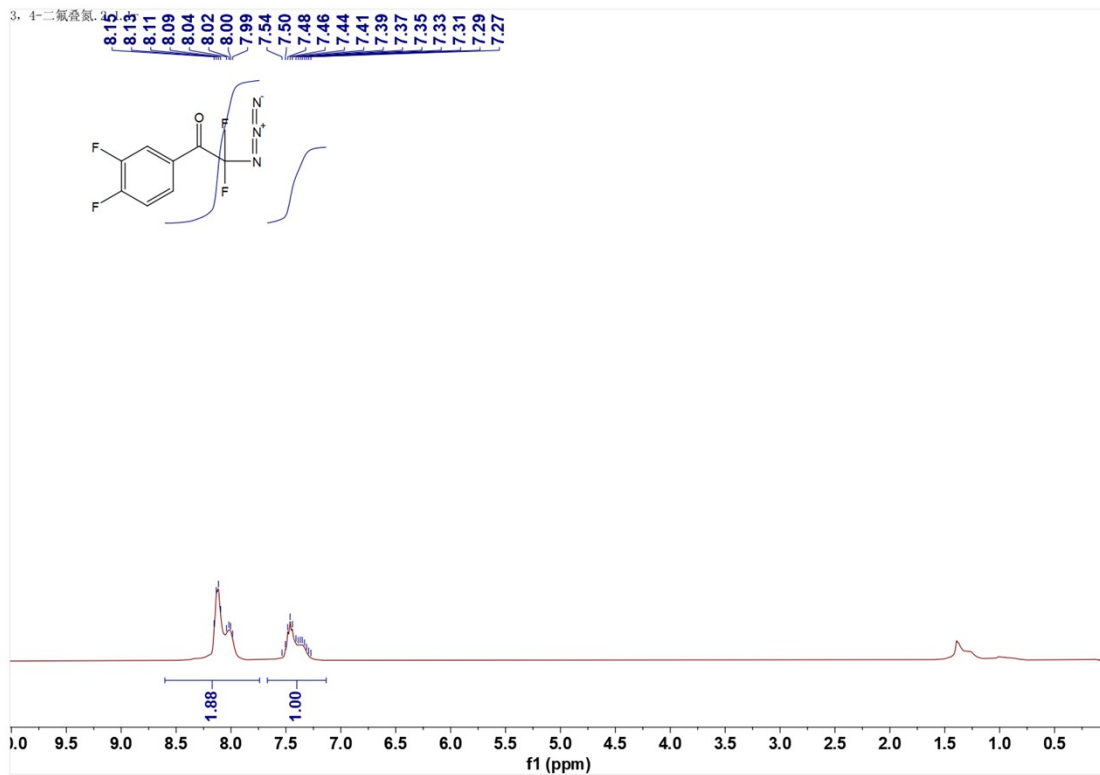
^1H NMR spectra of 2j



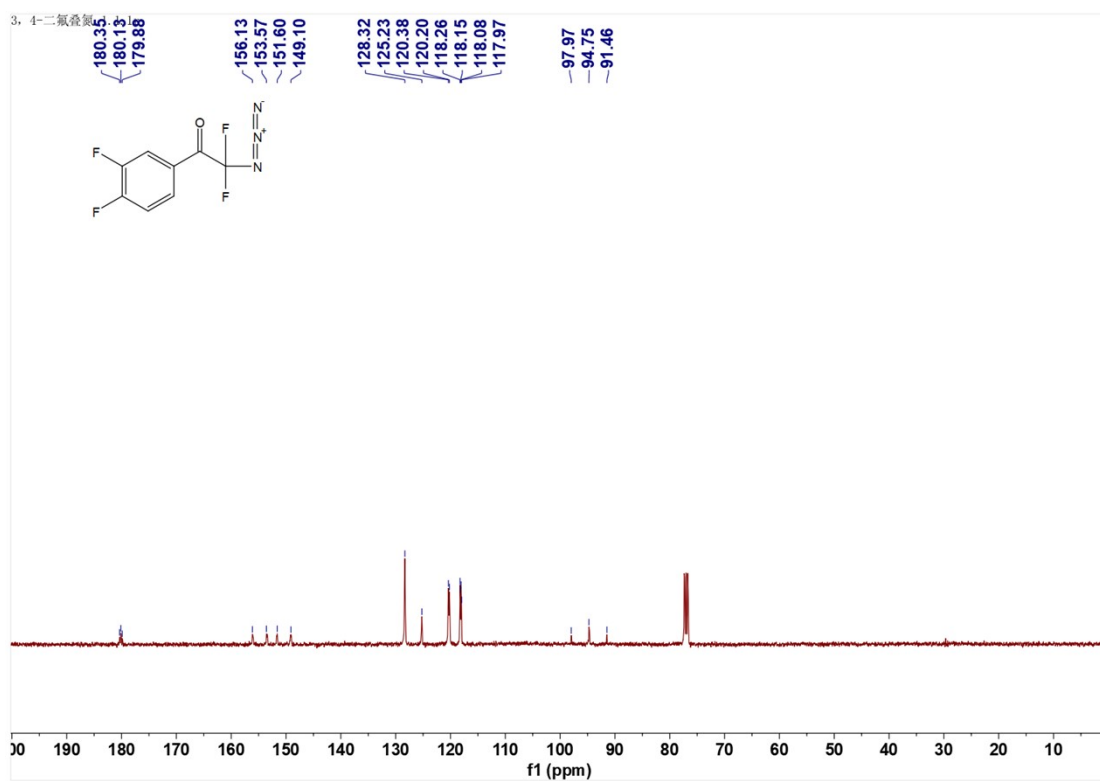
¹³C NMR spectra of 2j



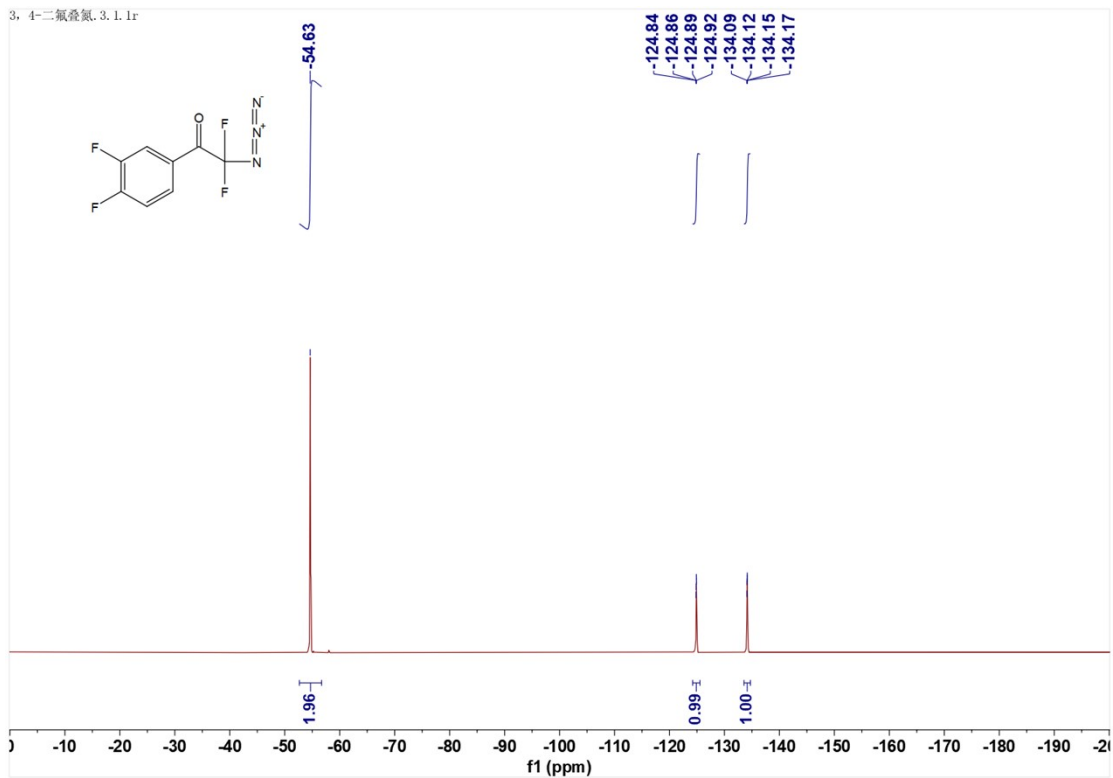
¹⁹F NMR spectra of 2j



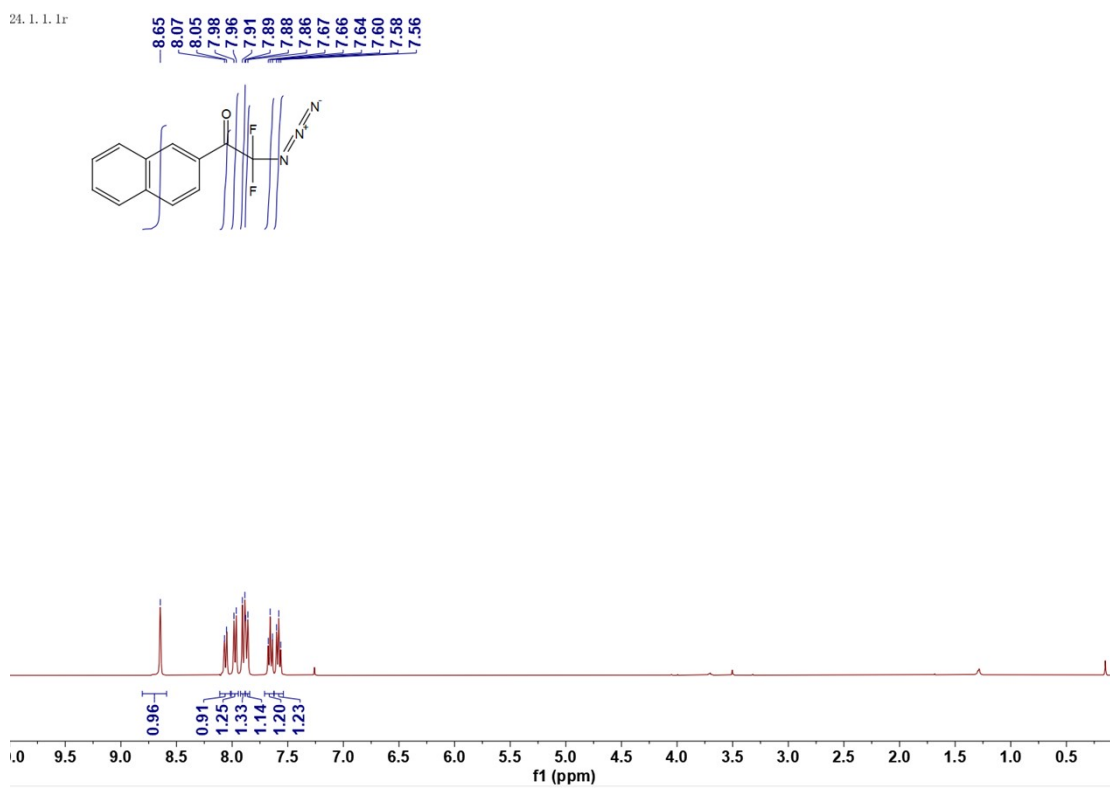
^1H NMR spectra of 2k



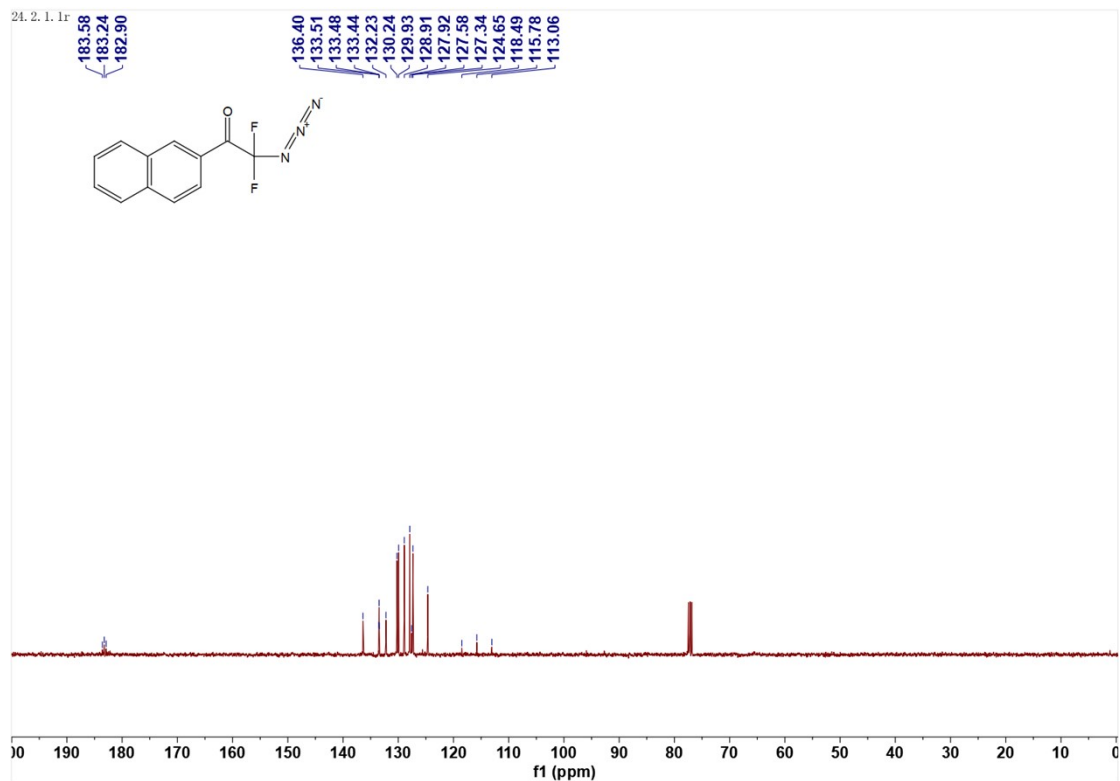
^{13}C NMR spectra of 2k



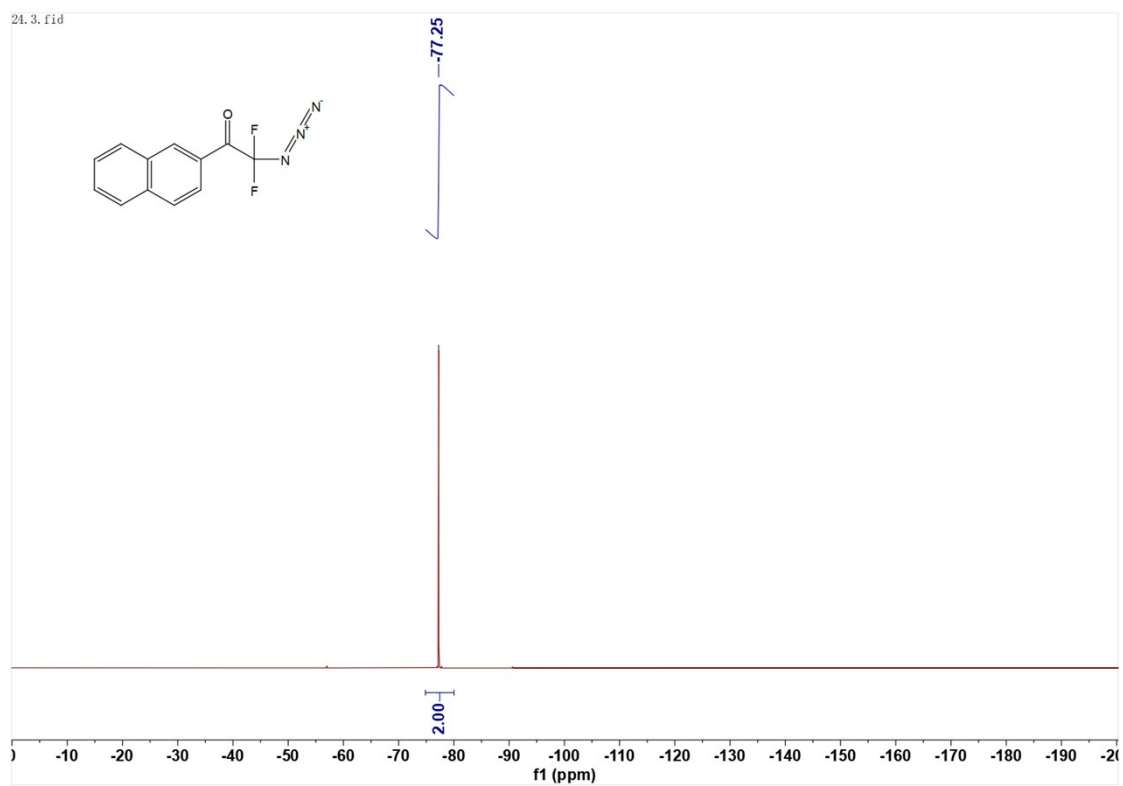
^{19}F NMR spectra of 2k



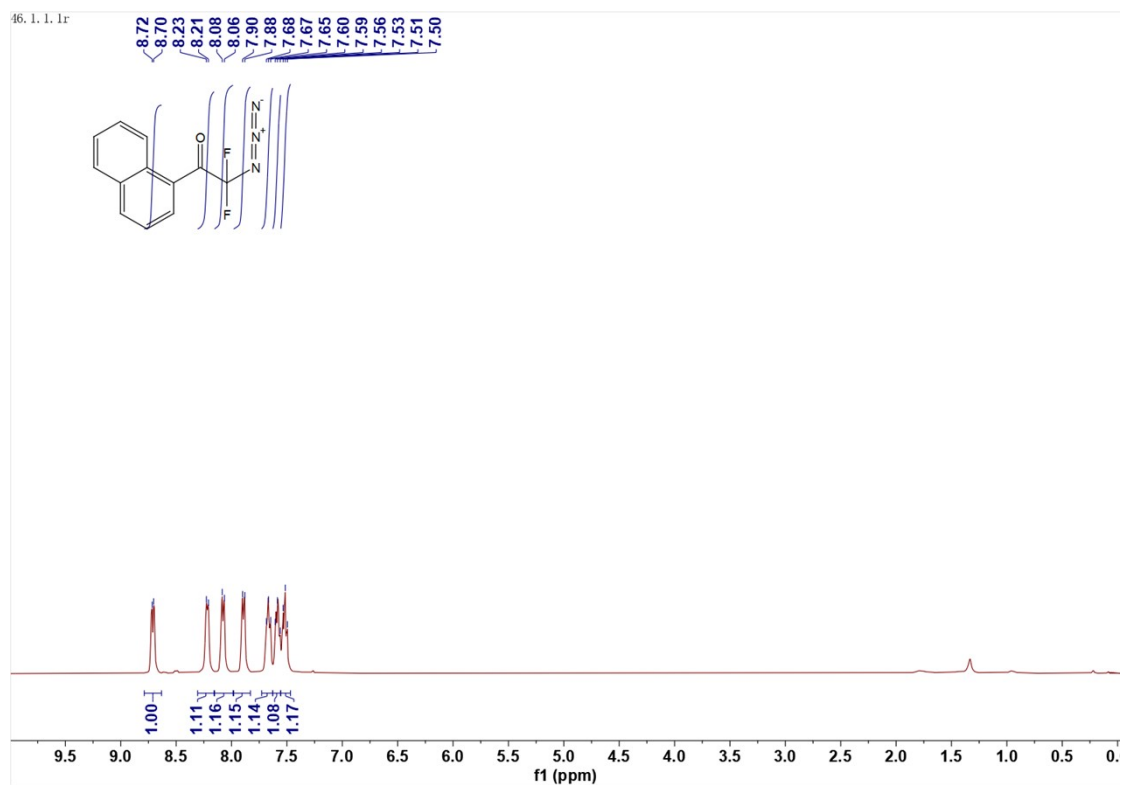
^1H NMR spectra of 2l



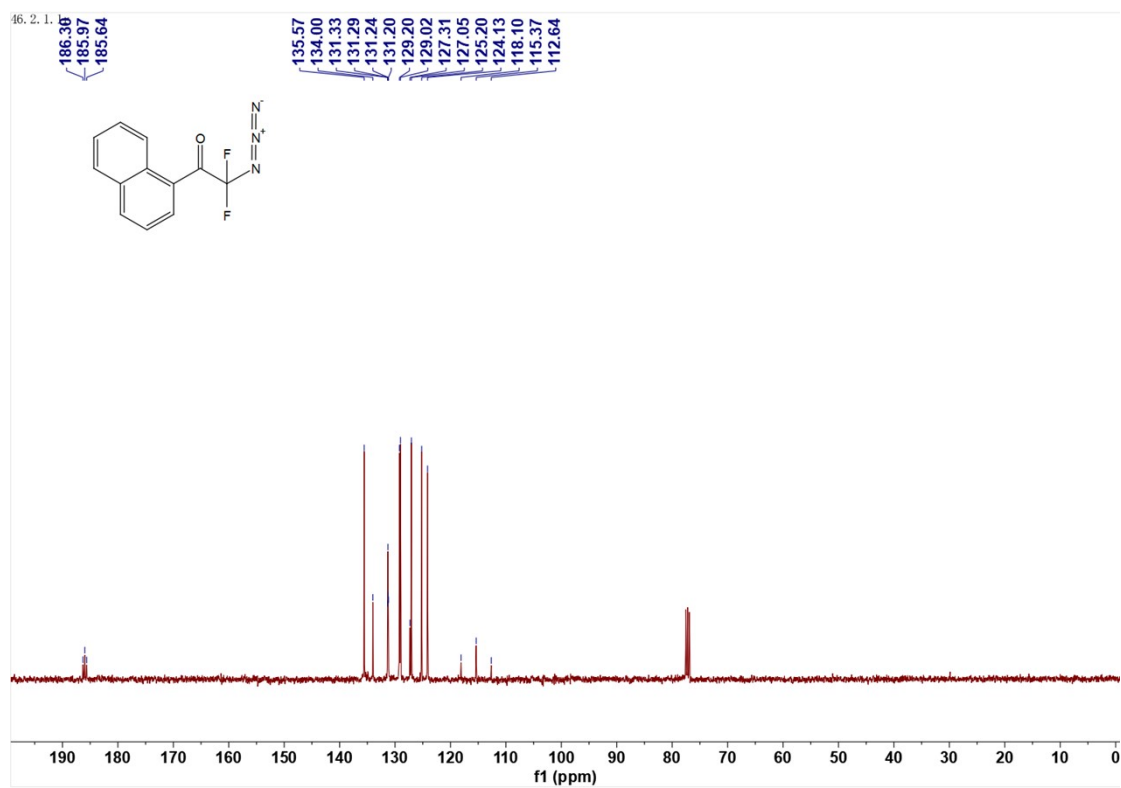
¹³C NMR spectra of 21



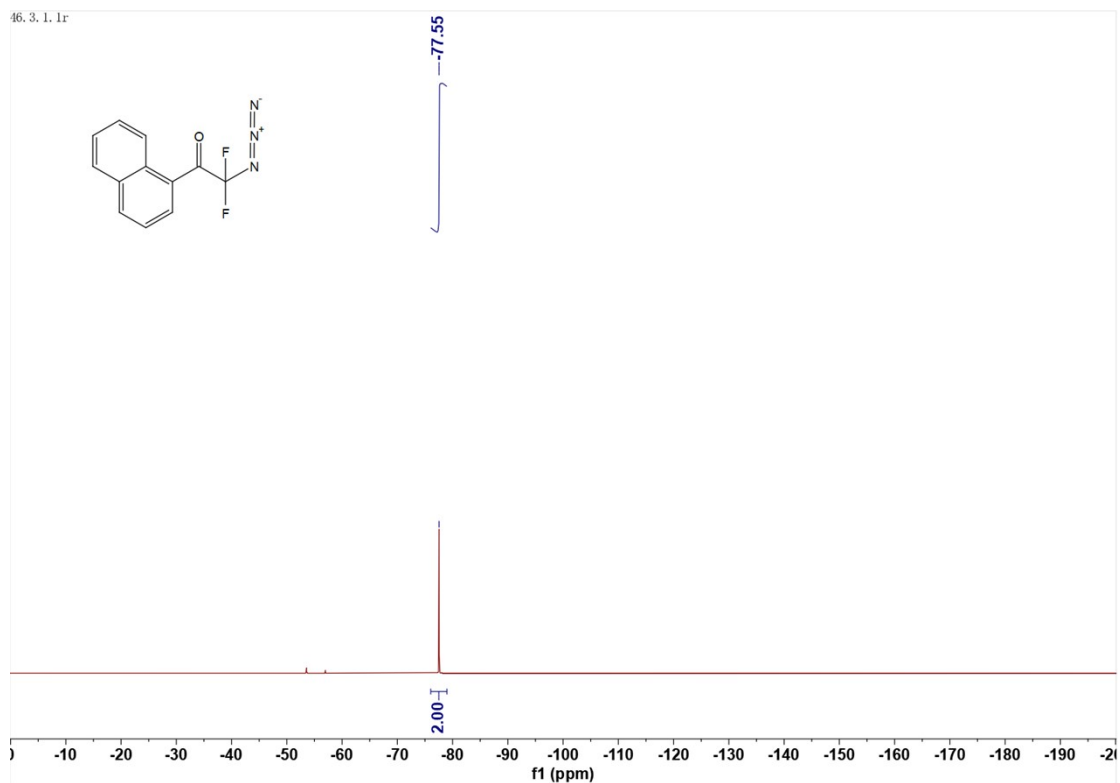
¹⁹F NMR spectra of 21



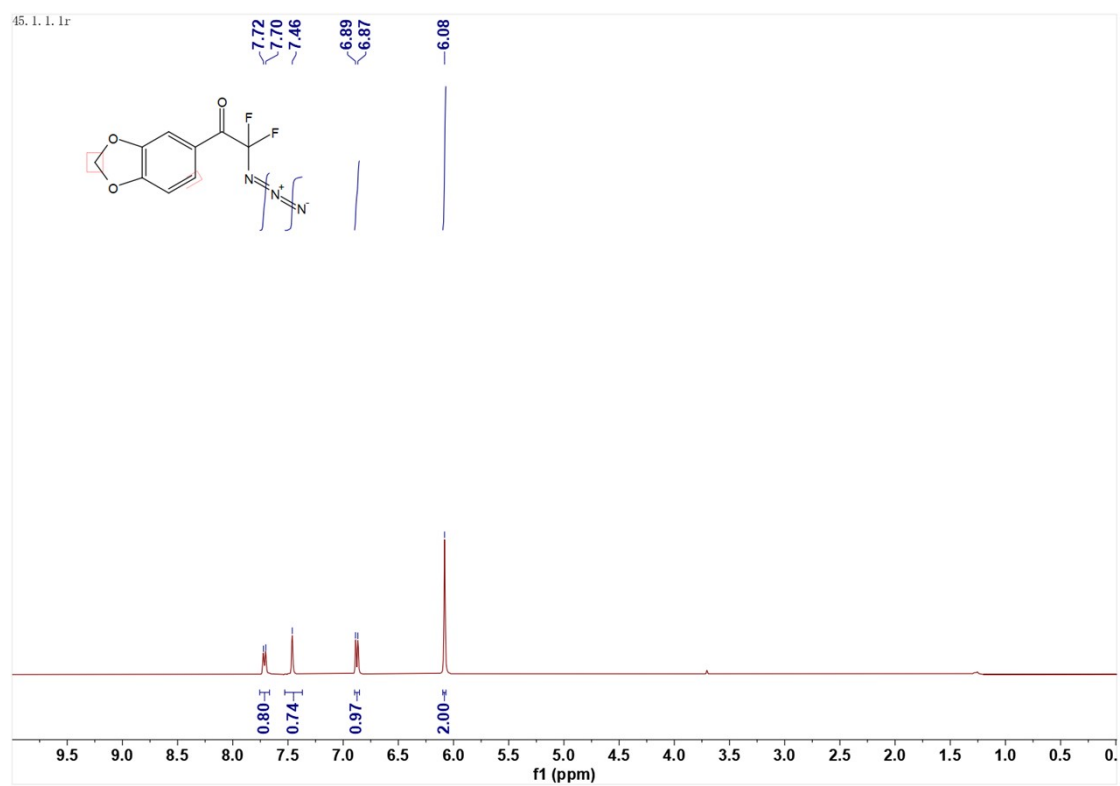
¹H NMR spectra of 2m



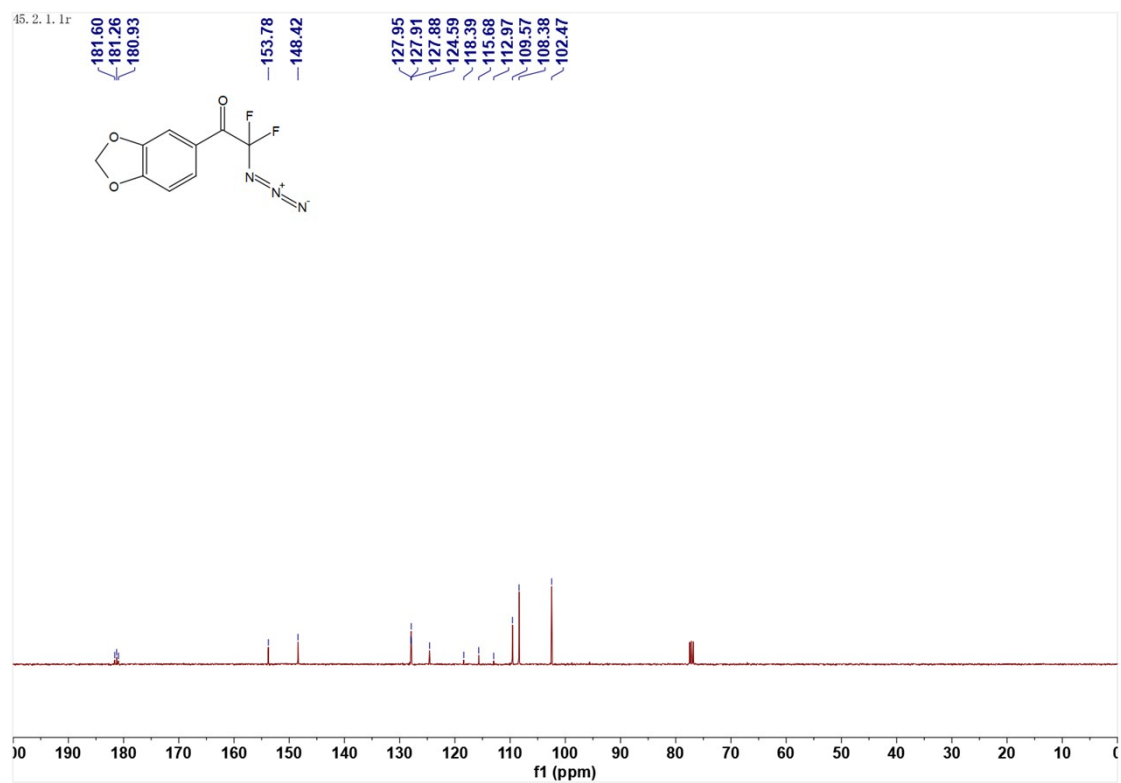
¹³C NMR spectra of 2m



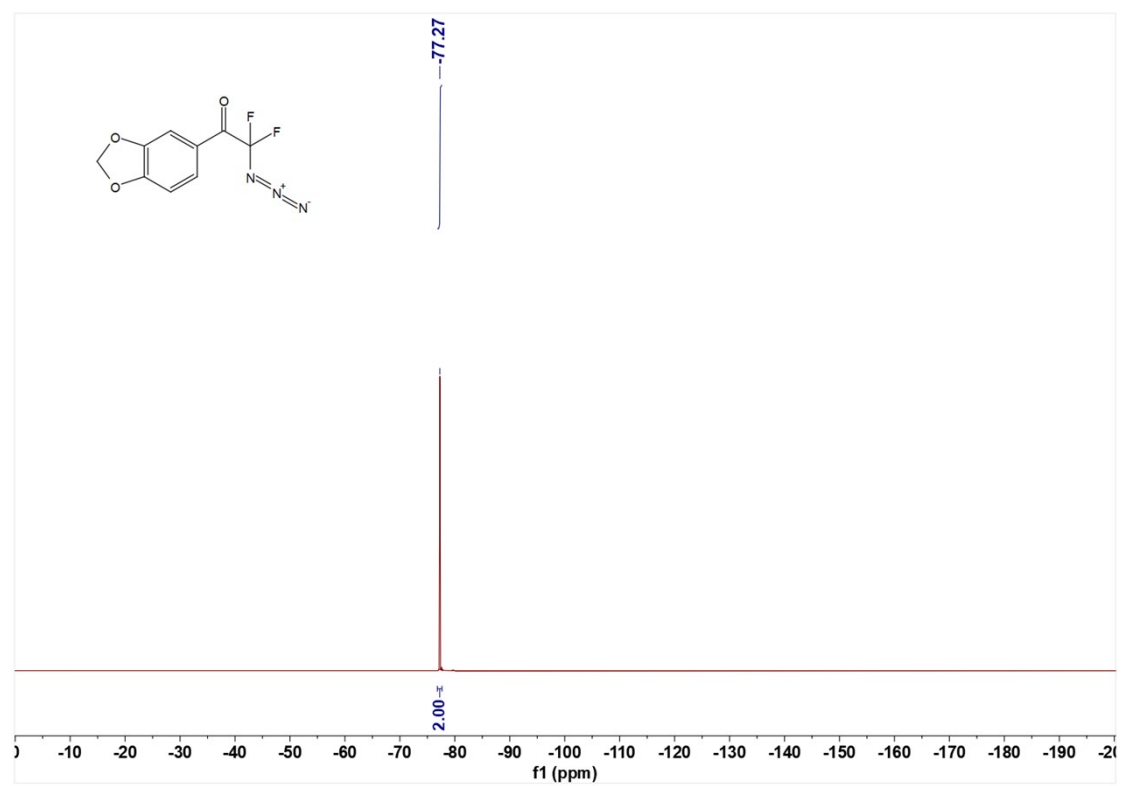
¹⁹F NMR spectra of 2m



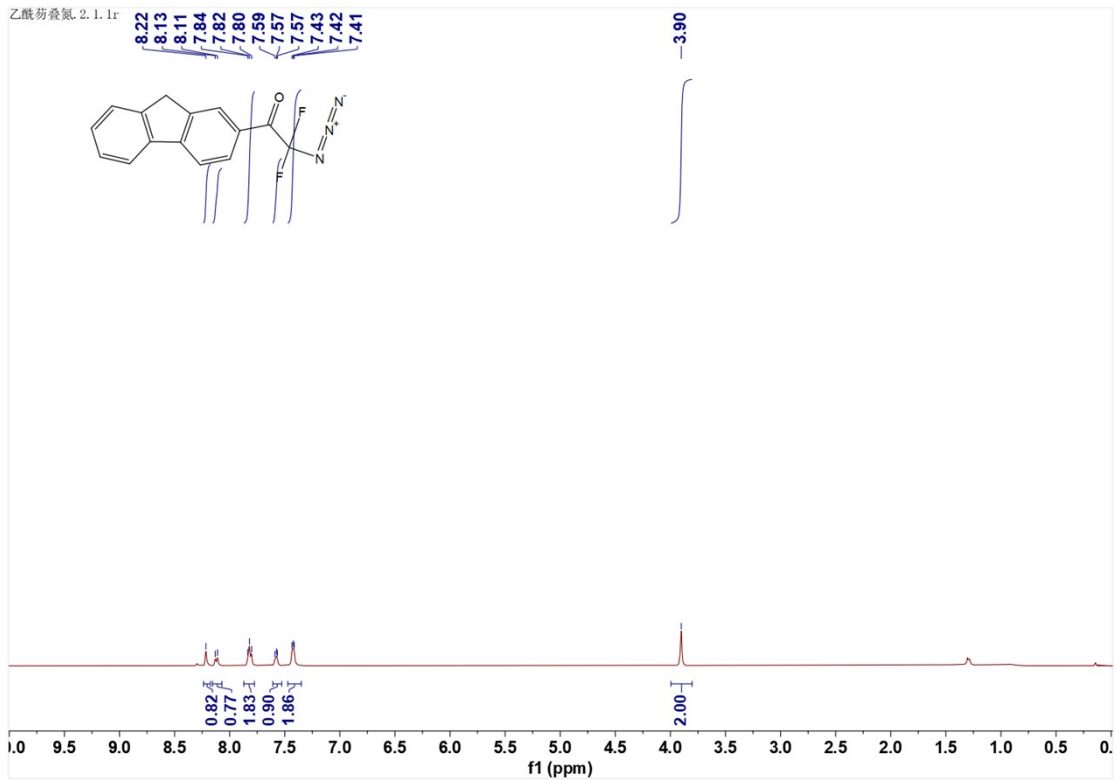
¹H NMR spectra of 2n



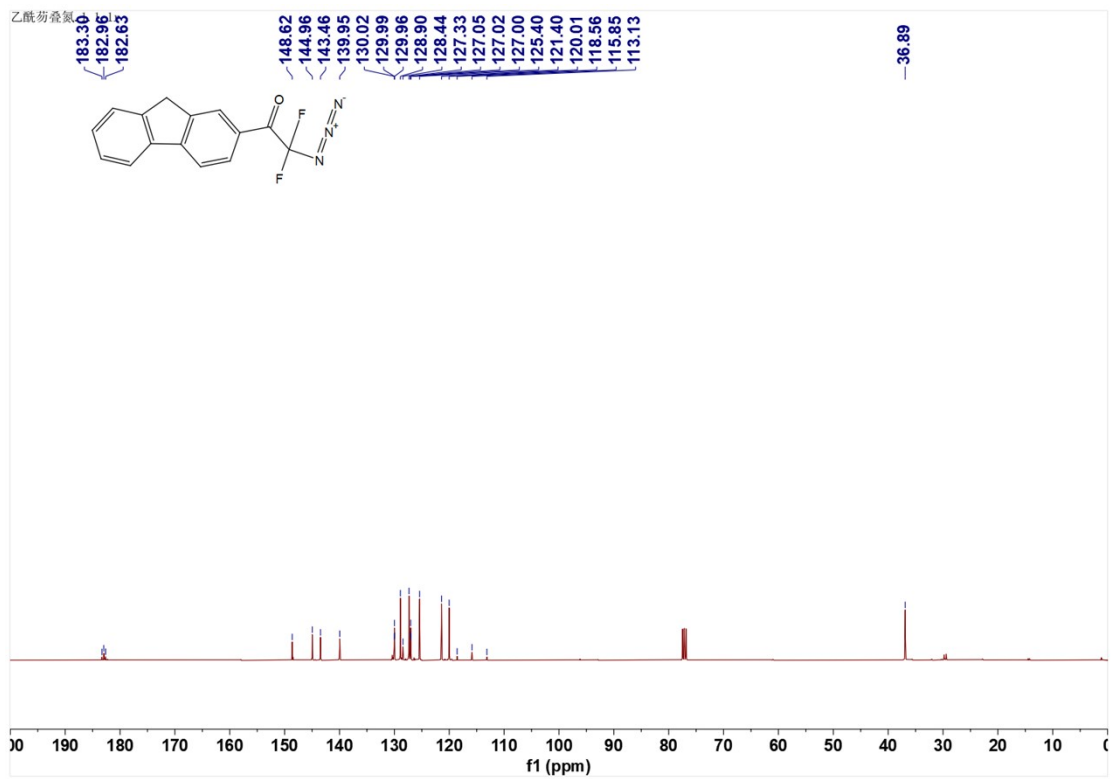
¹³C NMR spectra of 2n



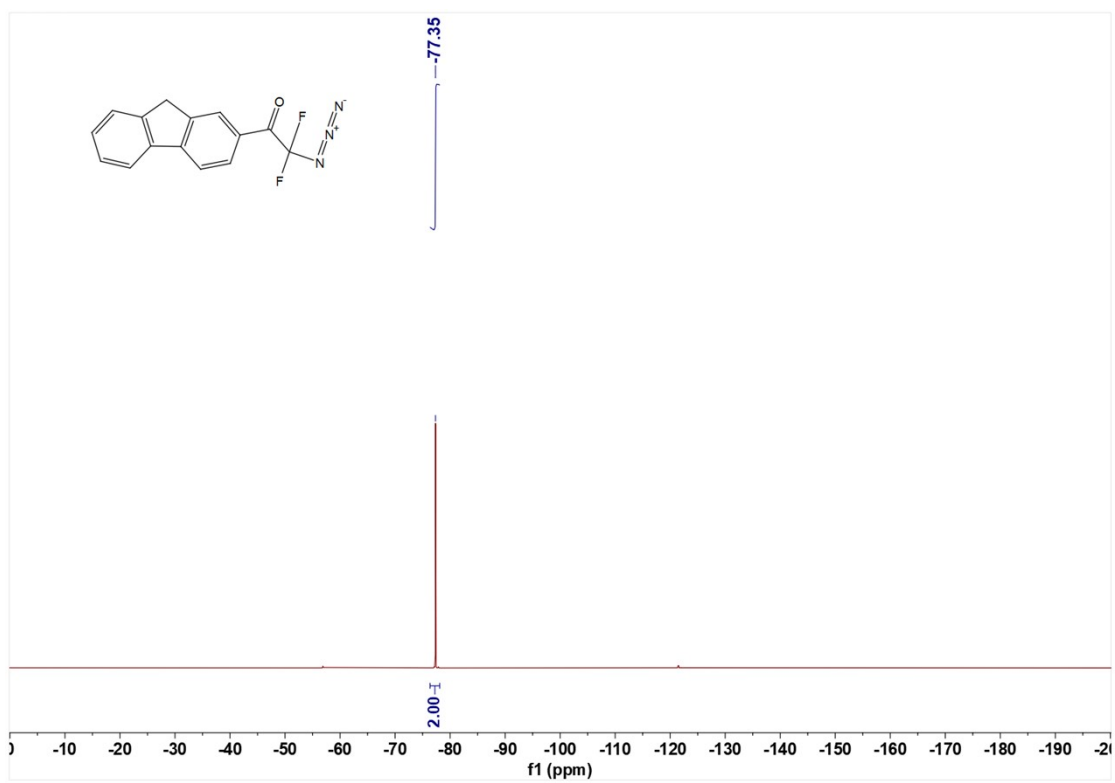
¹⁹F NMR spectra of 2n



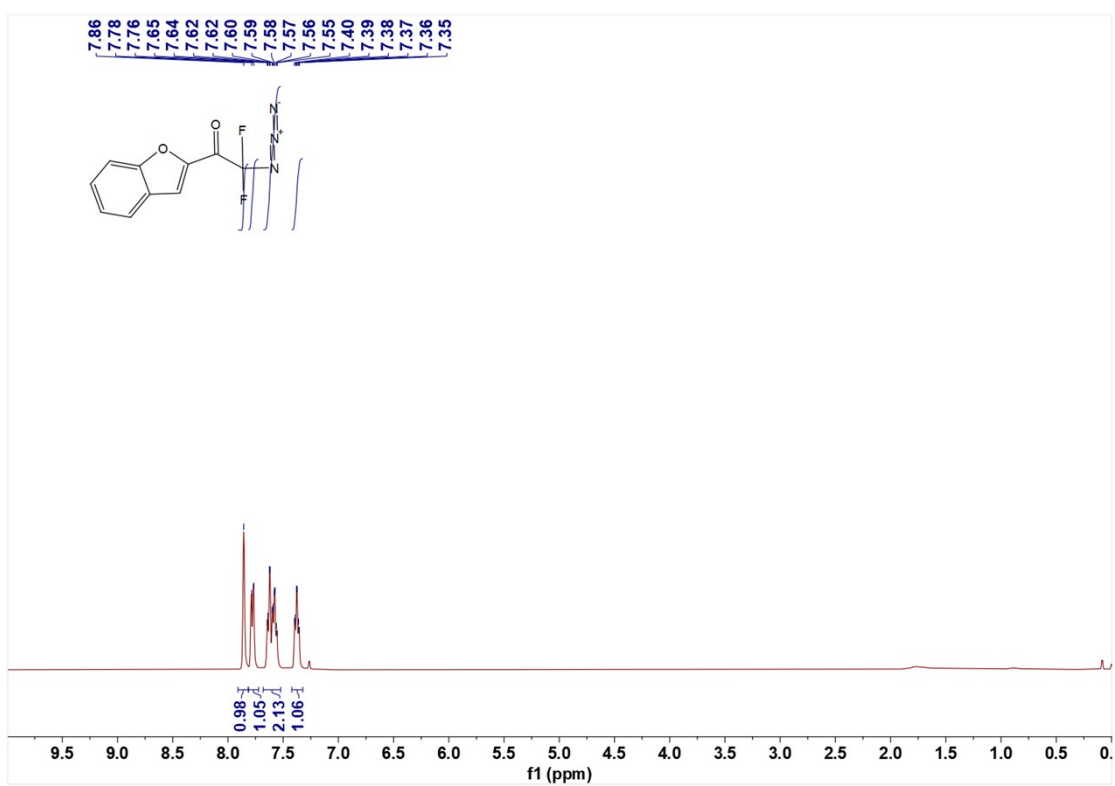
¹H NMR spectra of 2o



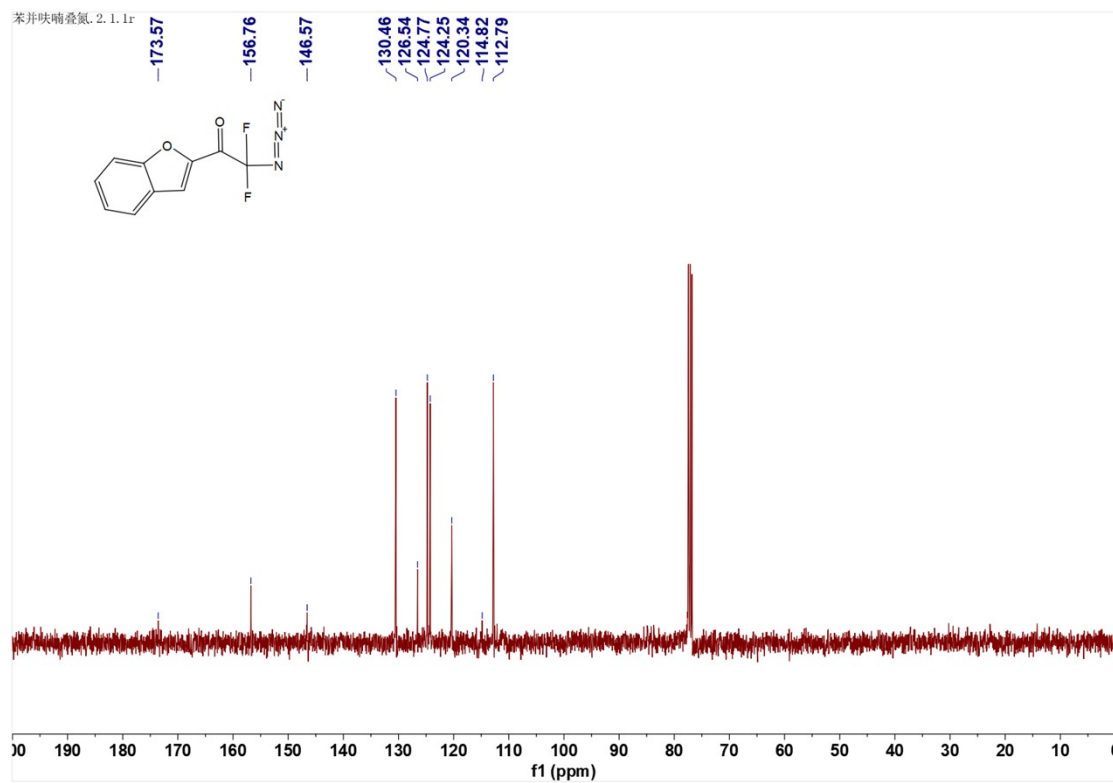
¹³C NMR spectra of 2o



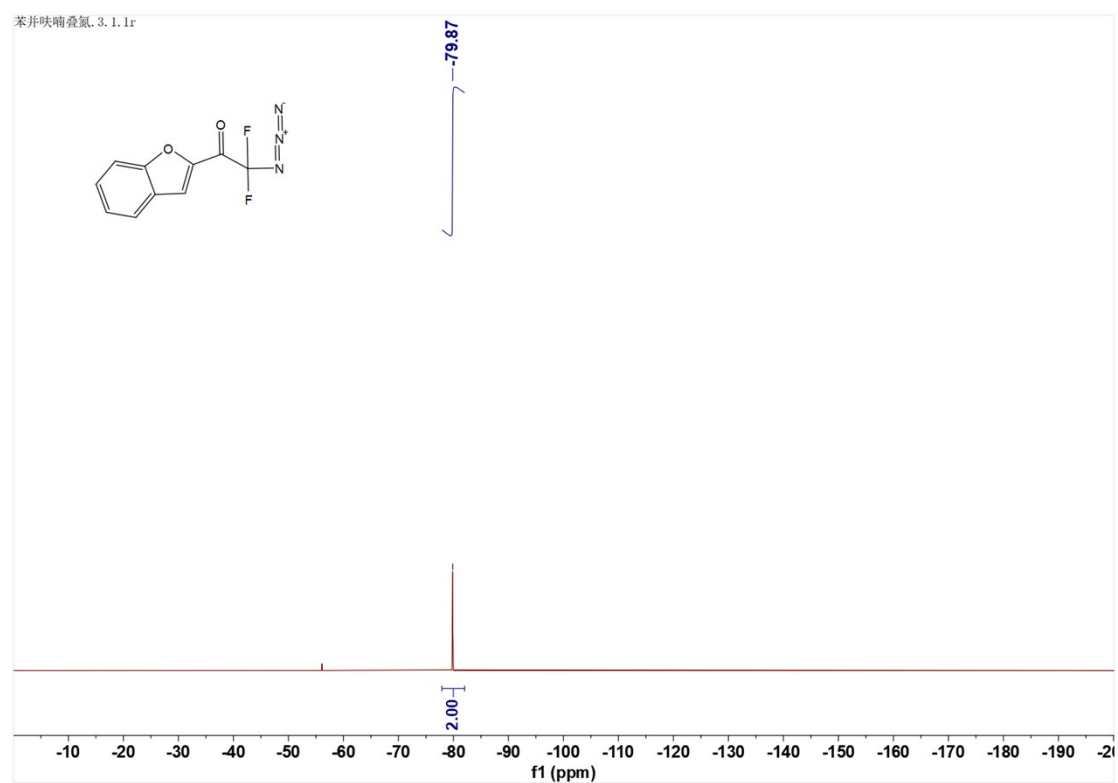
^{19}F NMR spectra of 2o



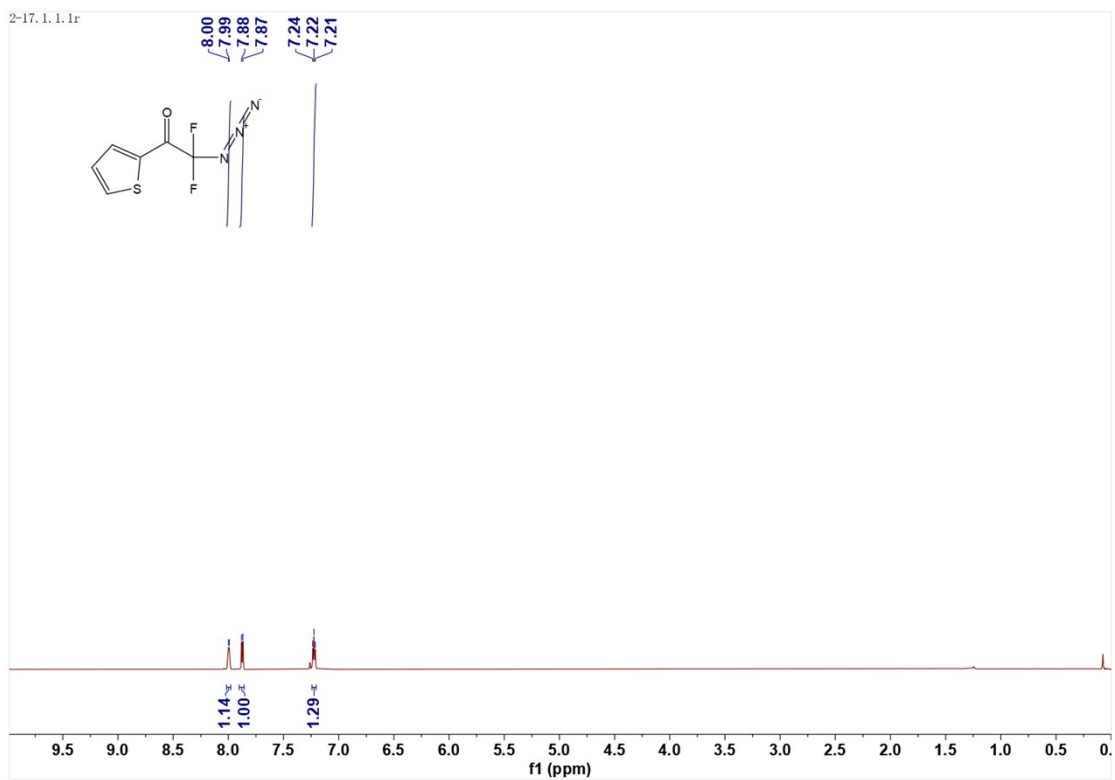
^1H NMR spectra of 2p



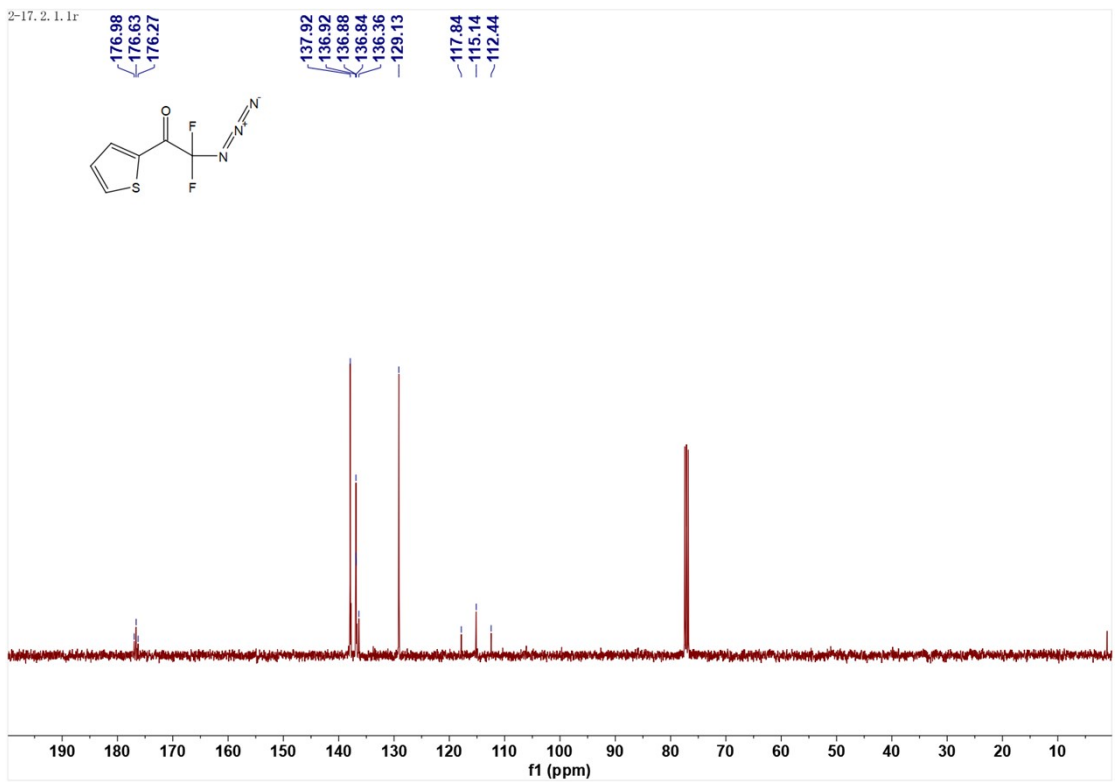
¹³C NMR spectra of 2p



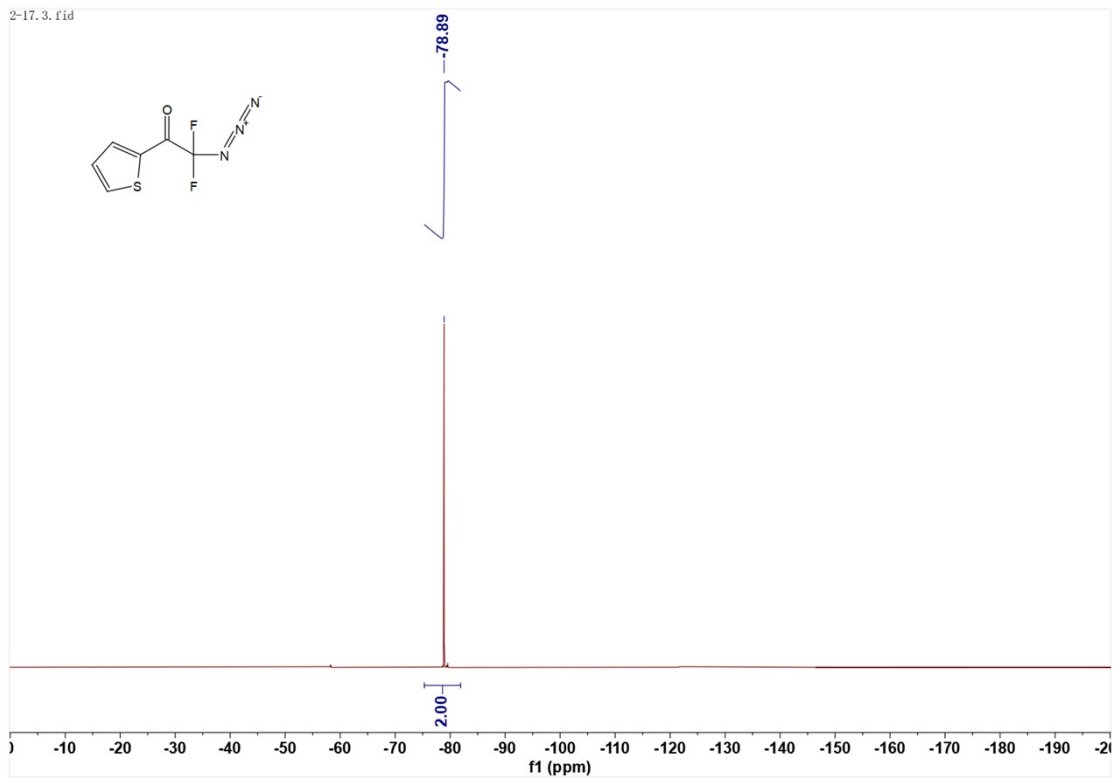
¹⁹F NMR spectra of 2p



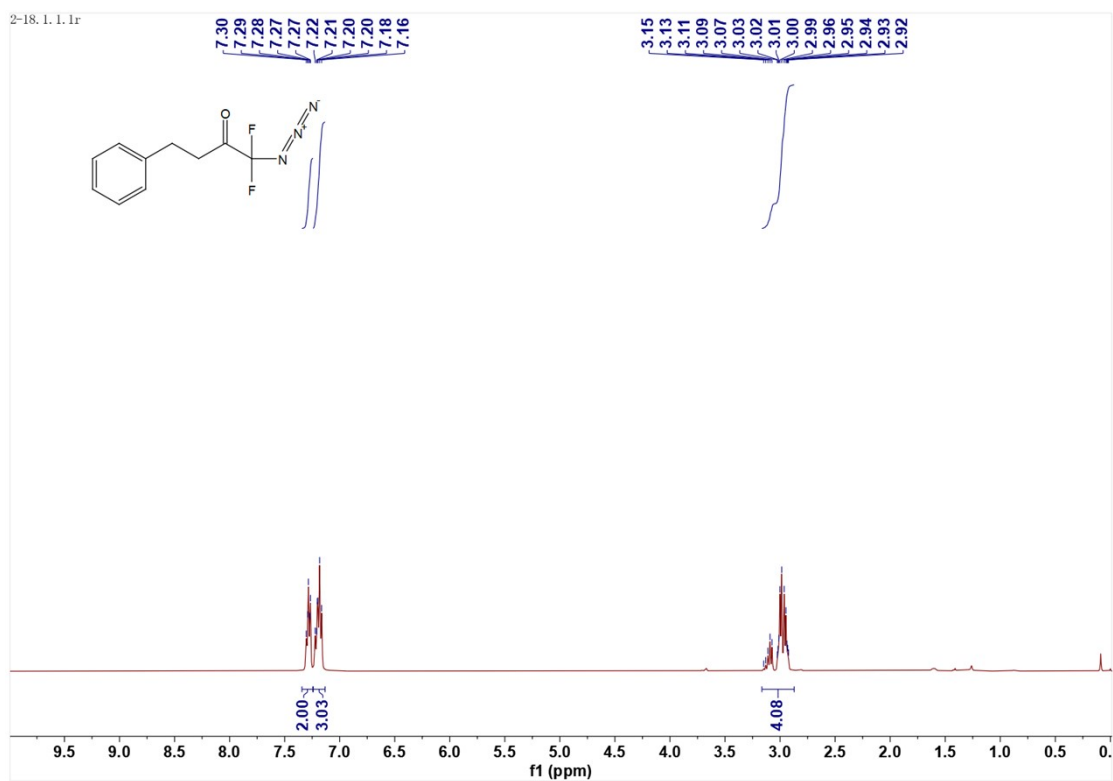
¹H NMR spectra of 2q



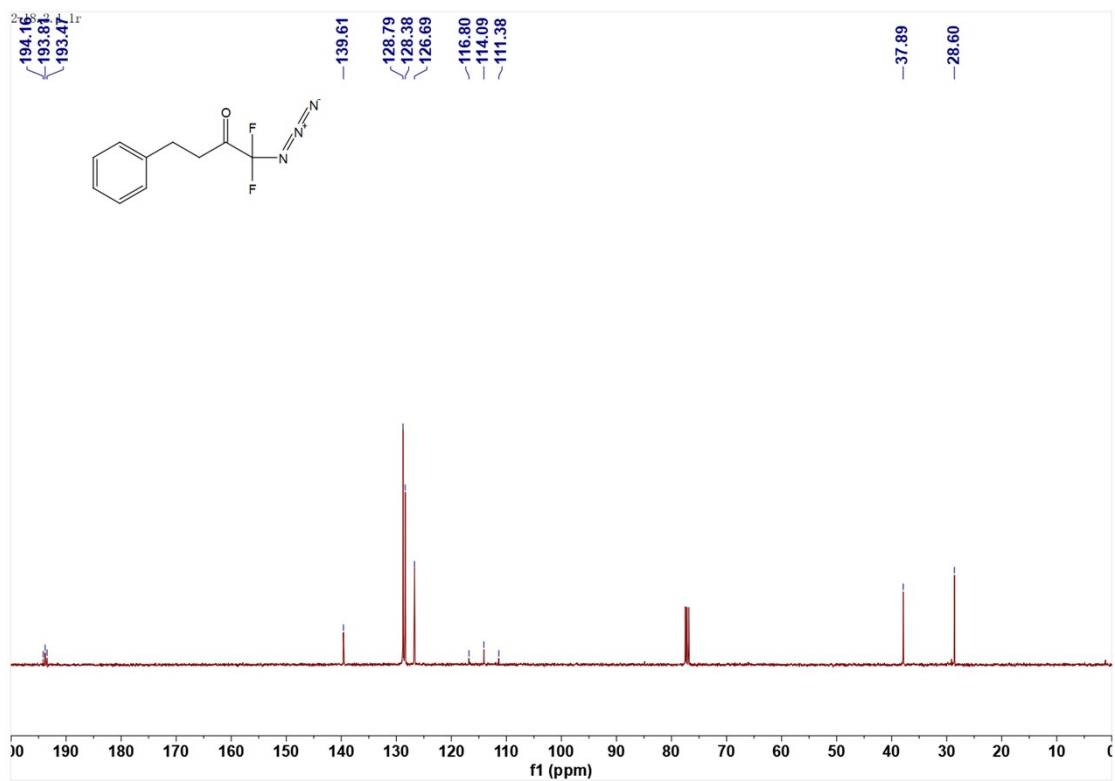
¹³C NMR spectra of 2q



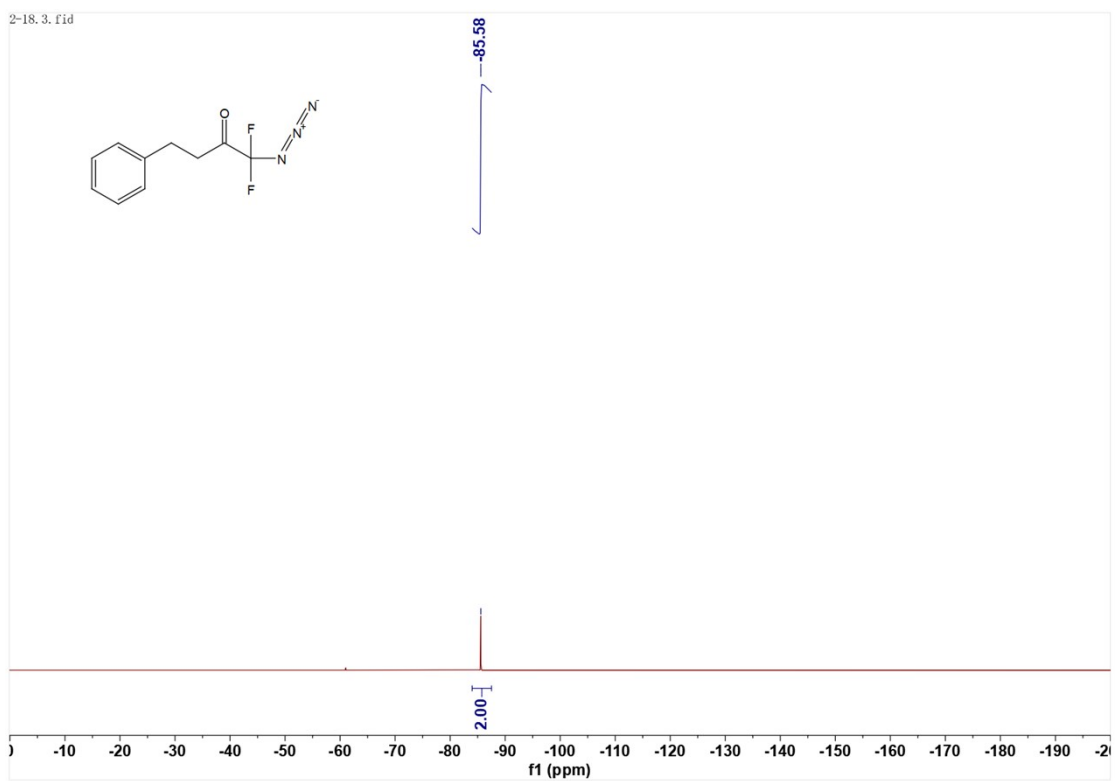
¹⁹F NMR spectra of 2q



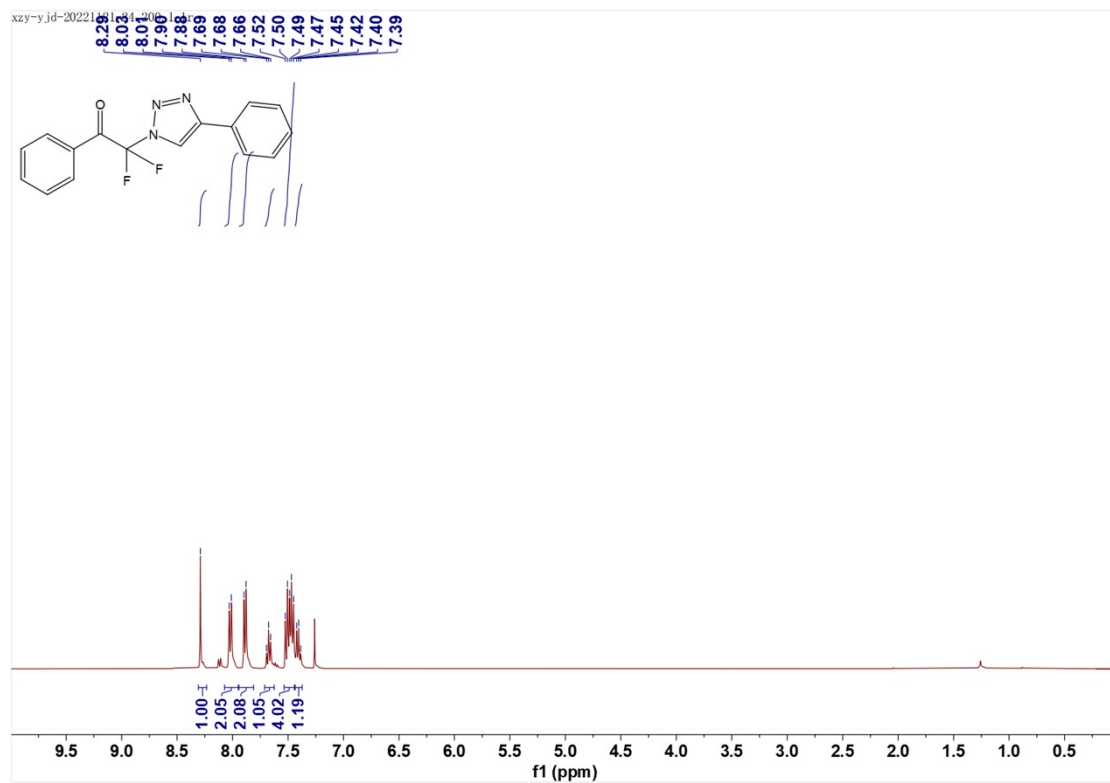
¹H NMR spectra of 2r



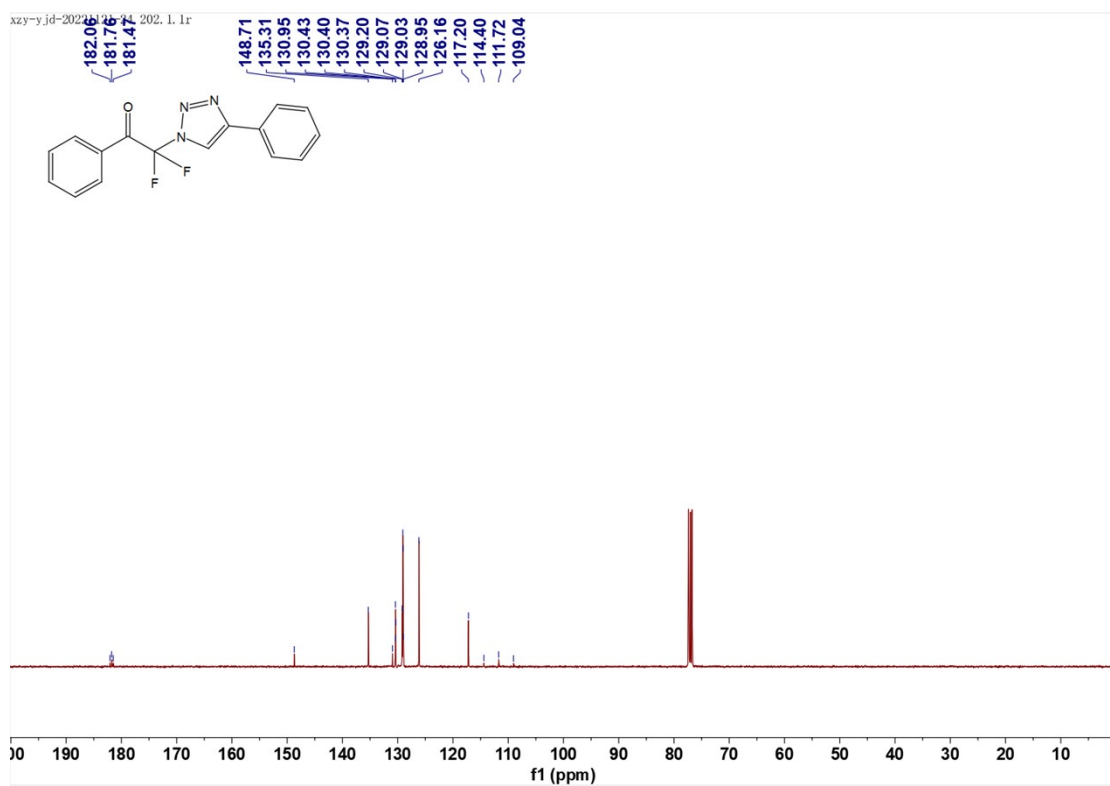
¹³C NMR spectra of 2r



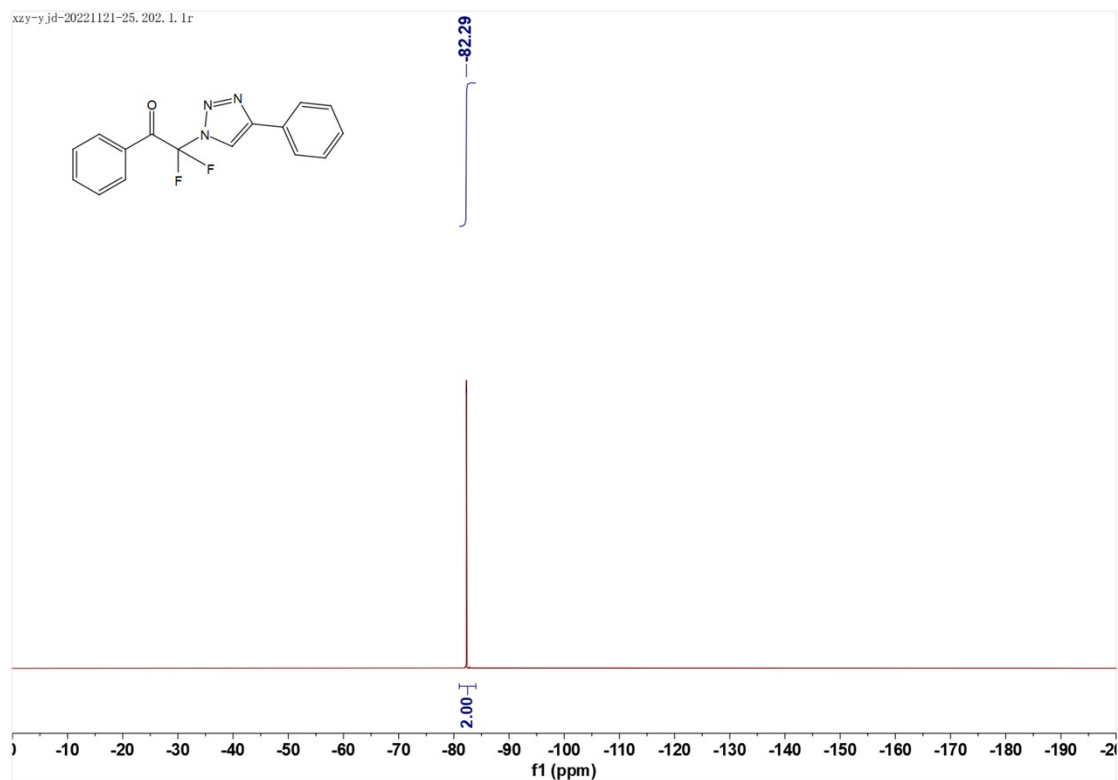
¹⁹F NMR spectra of 2r



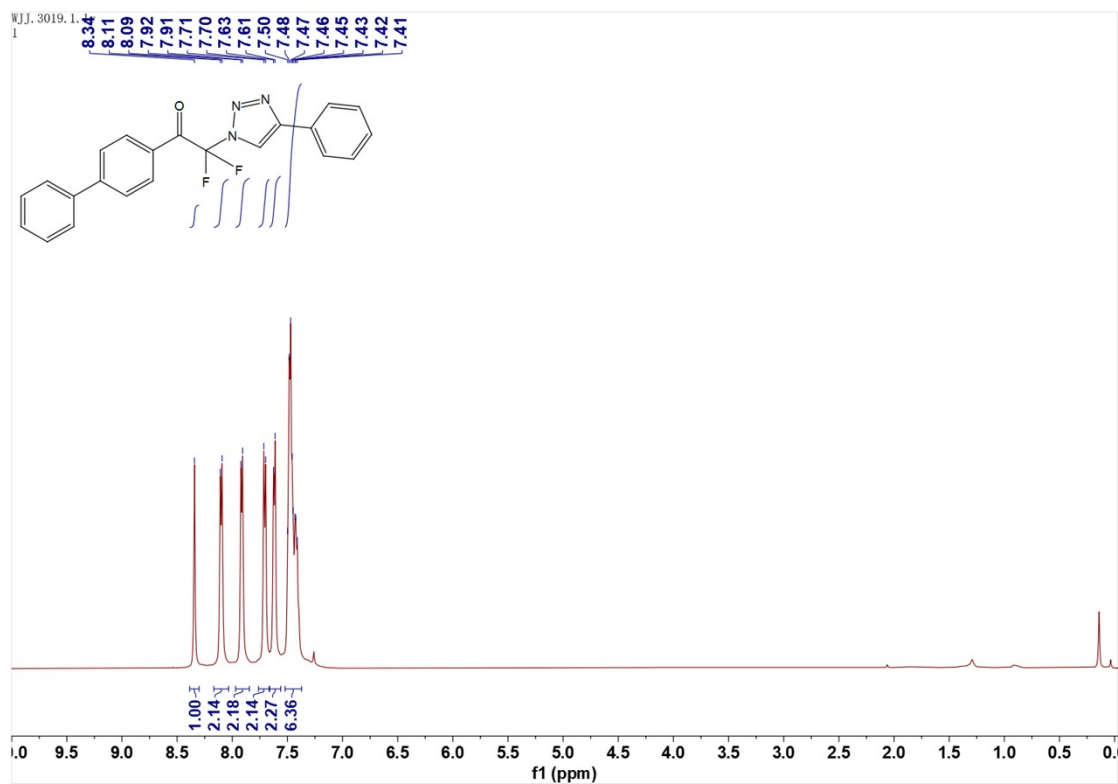
¹H NMR spectra of 4aa



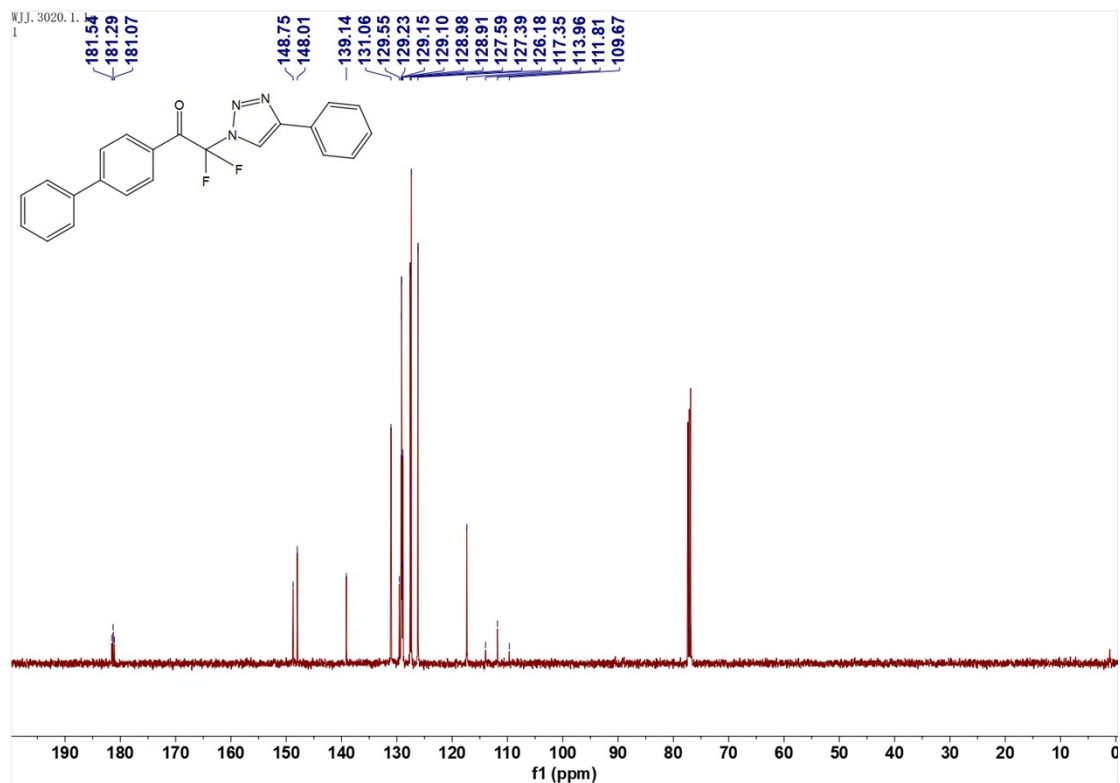
¹³C NMR spectra of 4aa



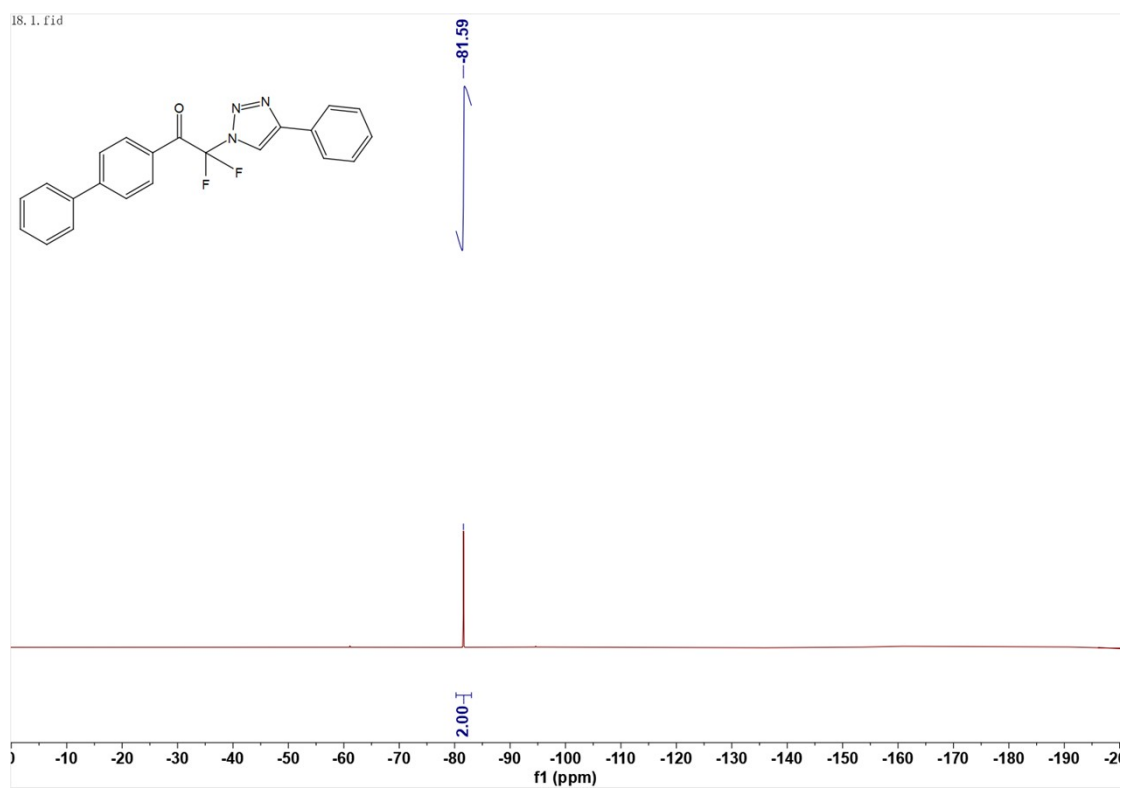
¹⁹F NMR spectra of 4aa



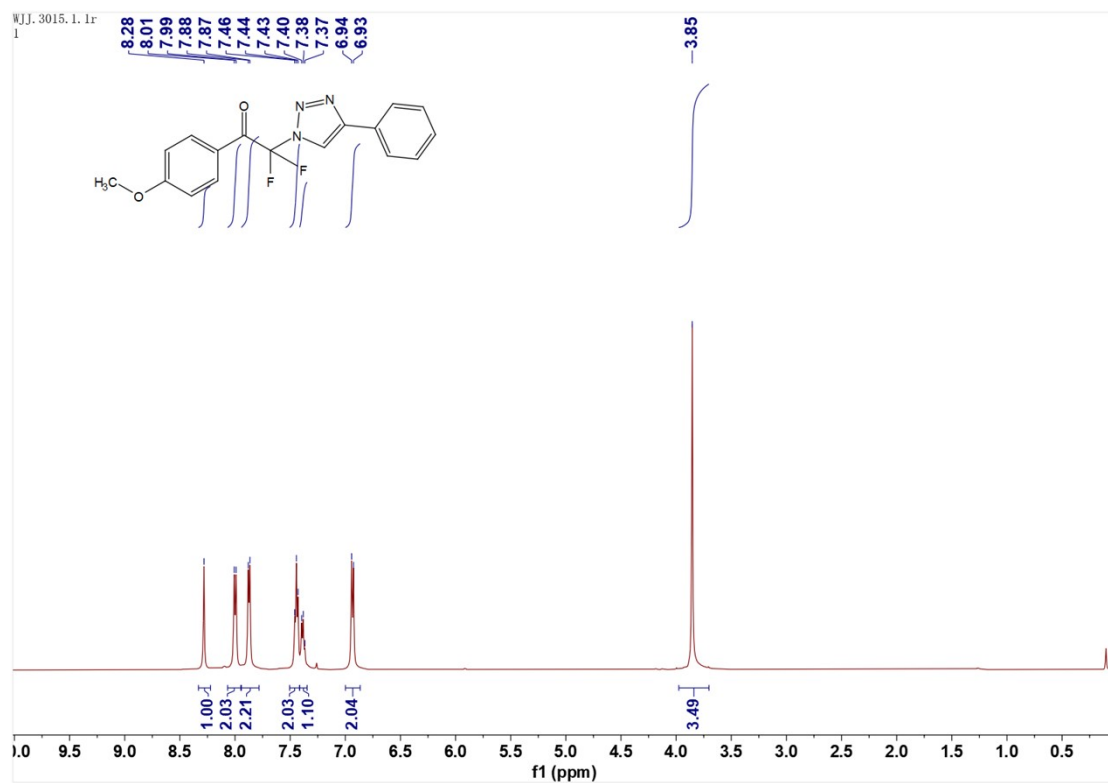
¹H NMR spectra of 4ba



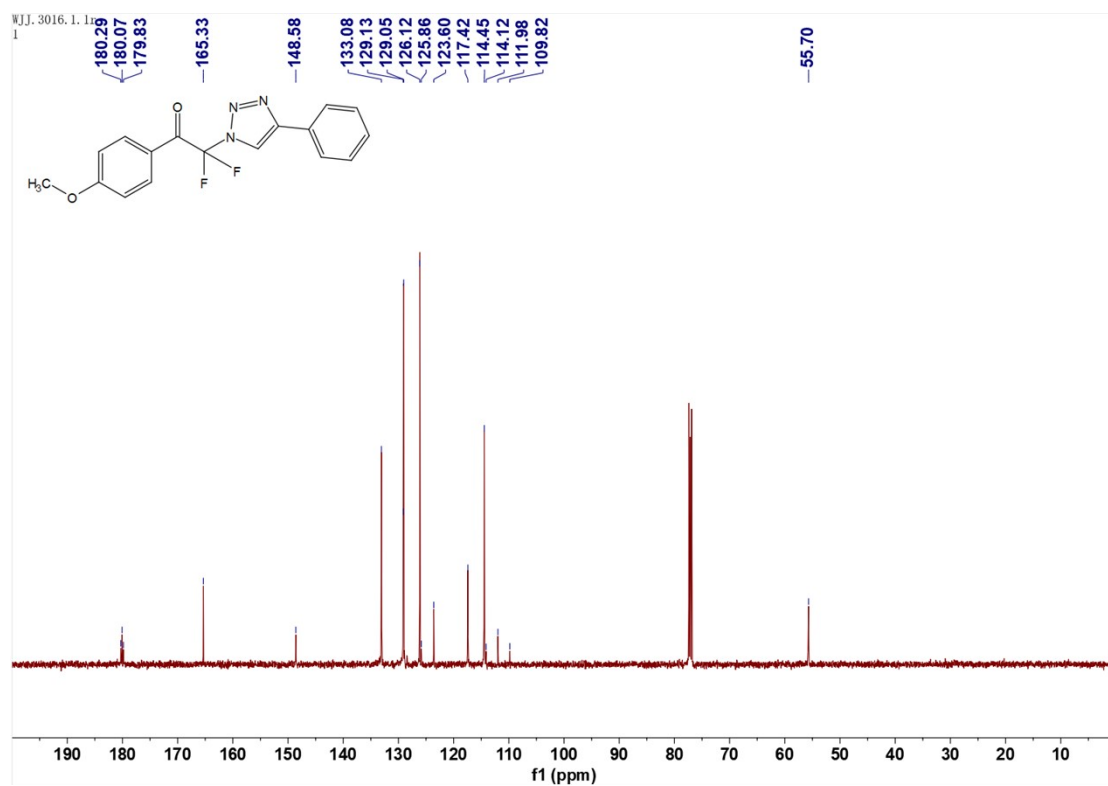
¹³C NMR spectra of 4ba



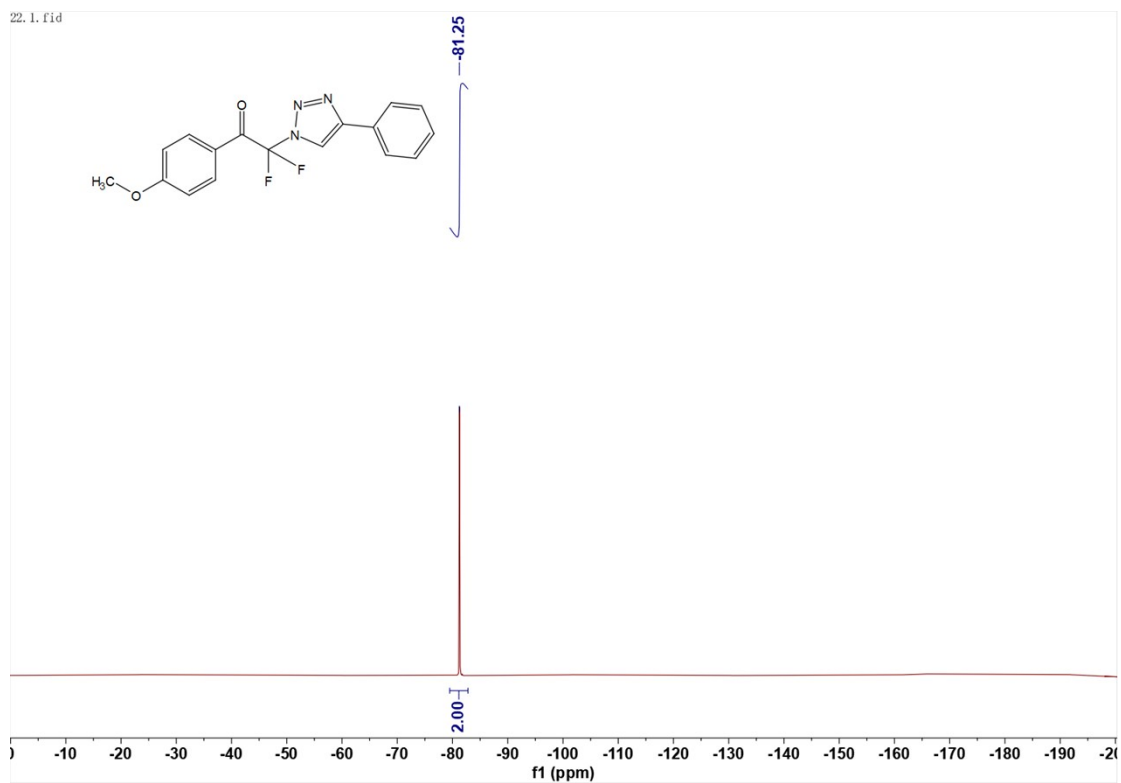
¹⁹F NMR spectra of 4ba



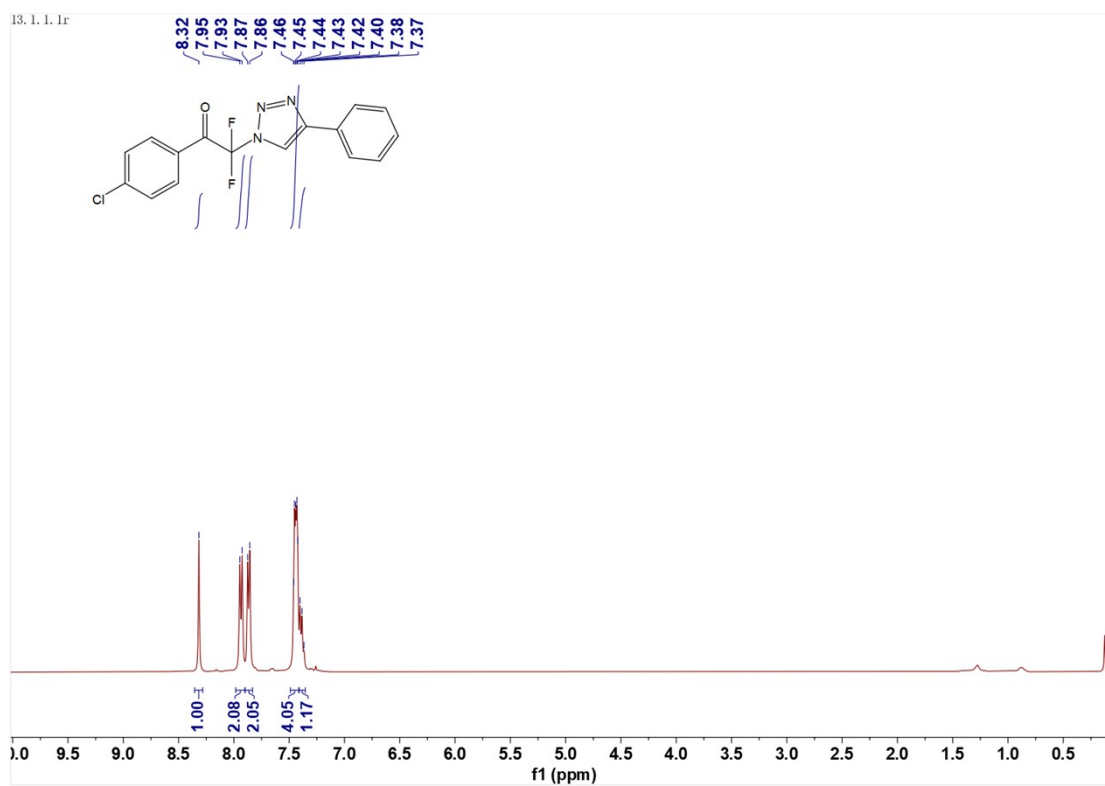
¹H NMR spectra of 4da



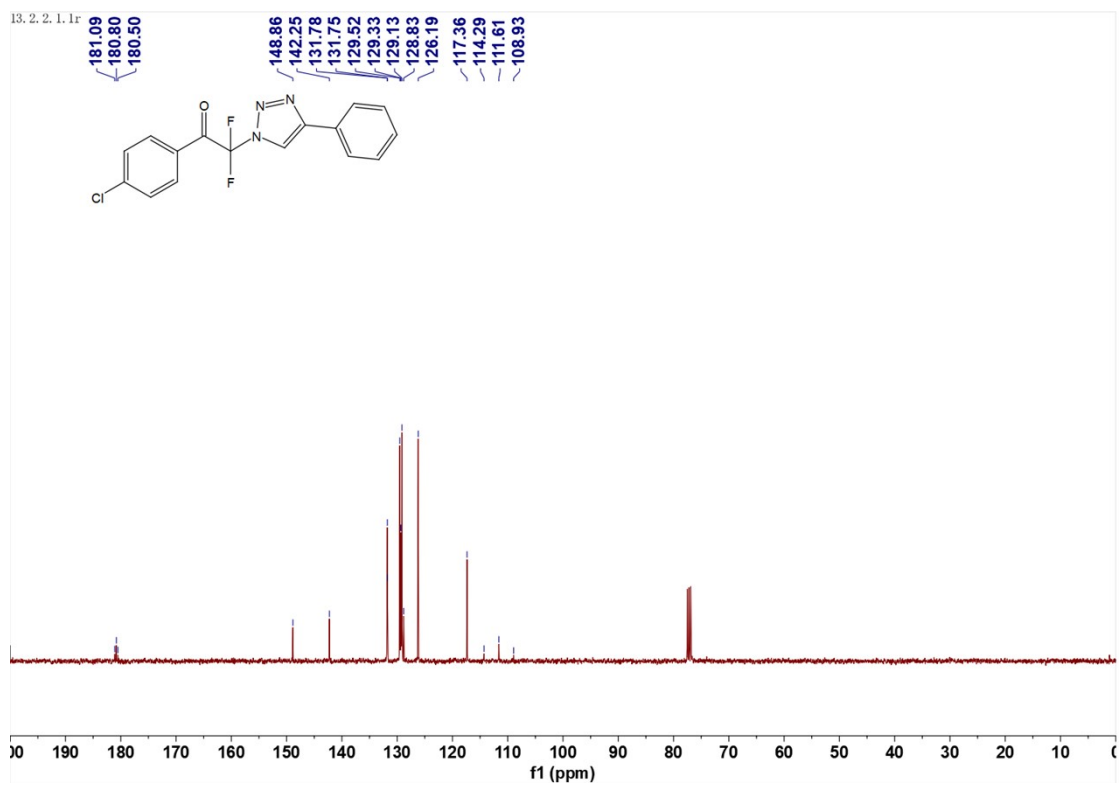
¹³C NMR spectra of 4da



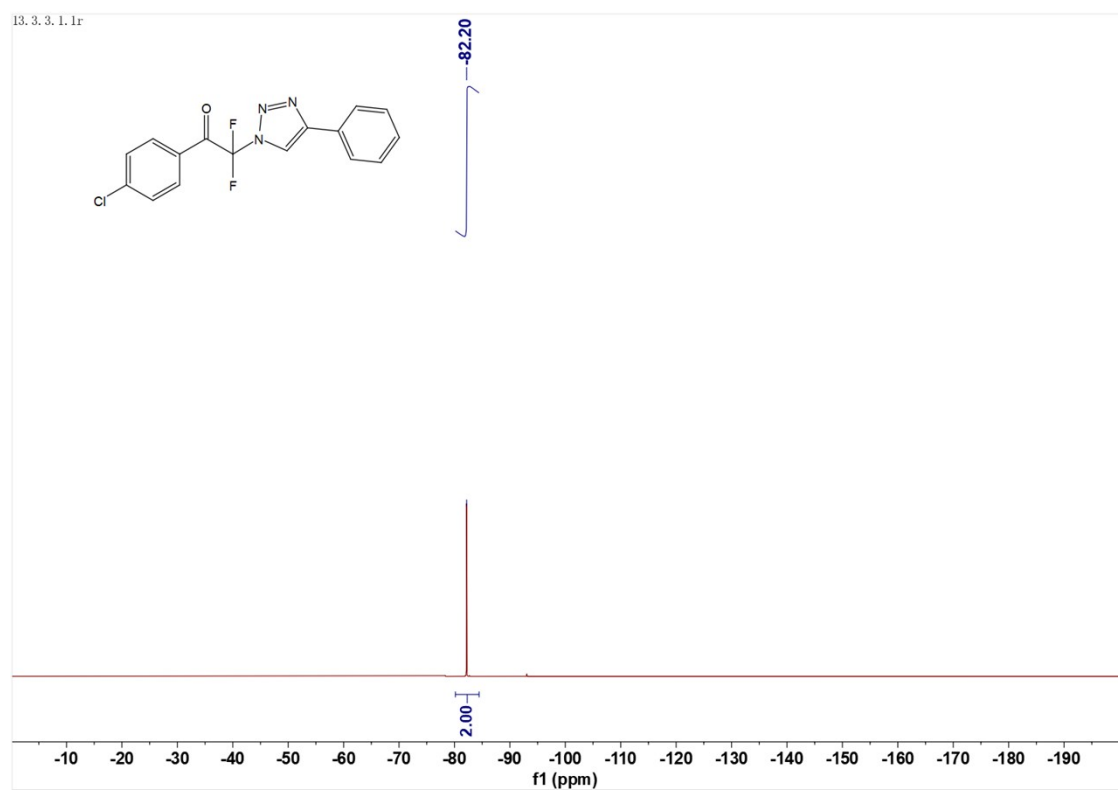
¹⁹F NMR spectra of 4da



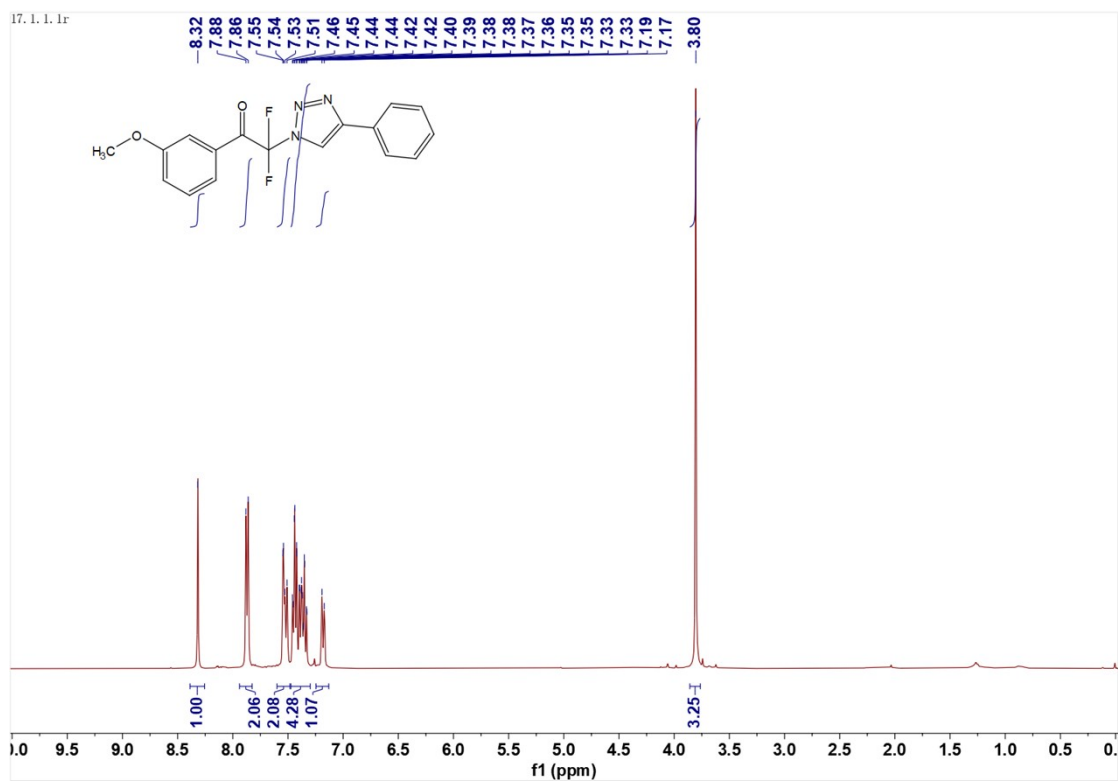
¹H NMR spectra of 4ea



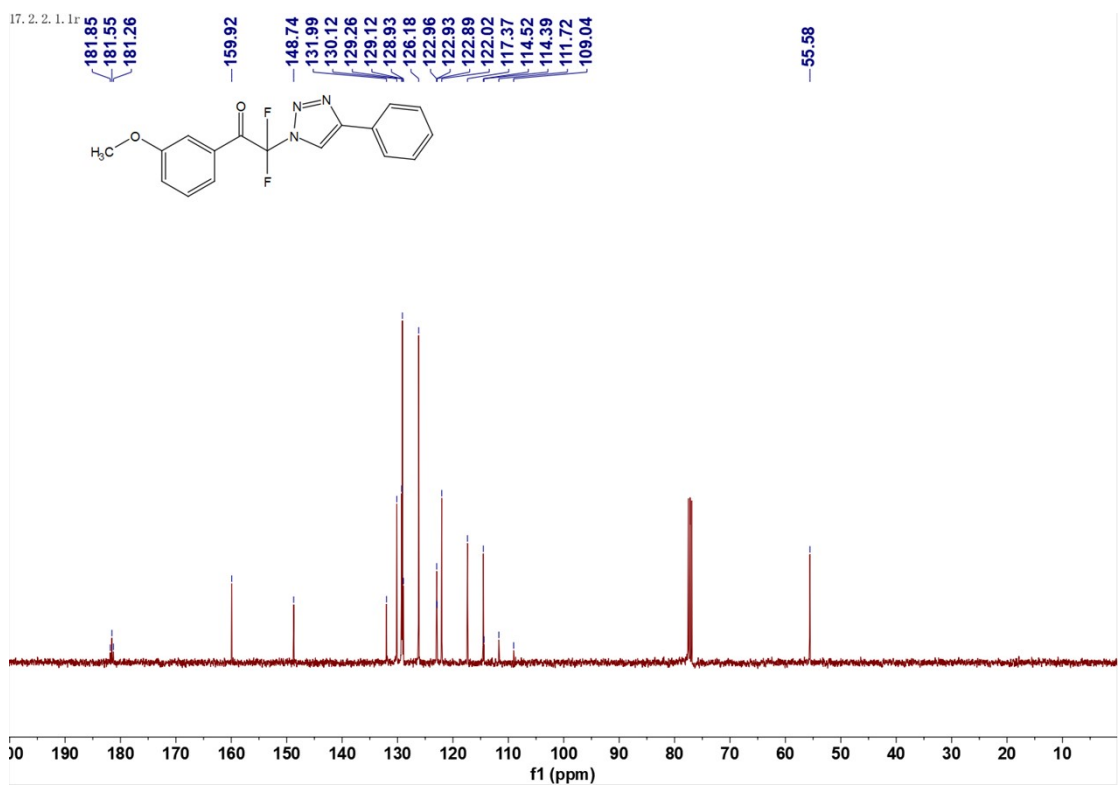
¹³C NMR spectra of 4ea



¹⁹F NMR spectra of 4ea

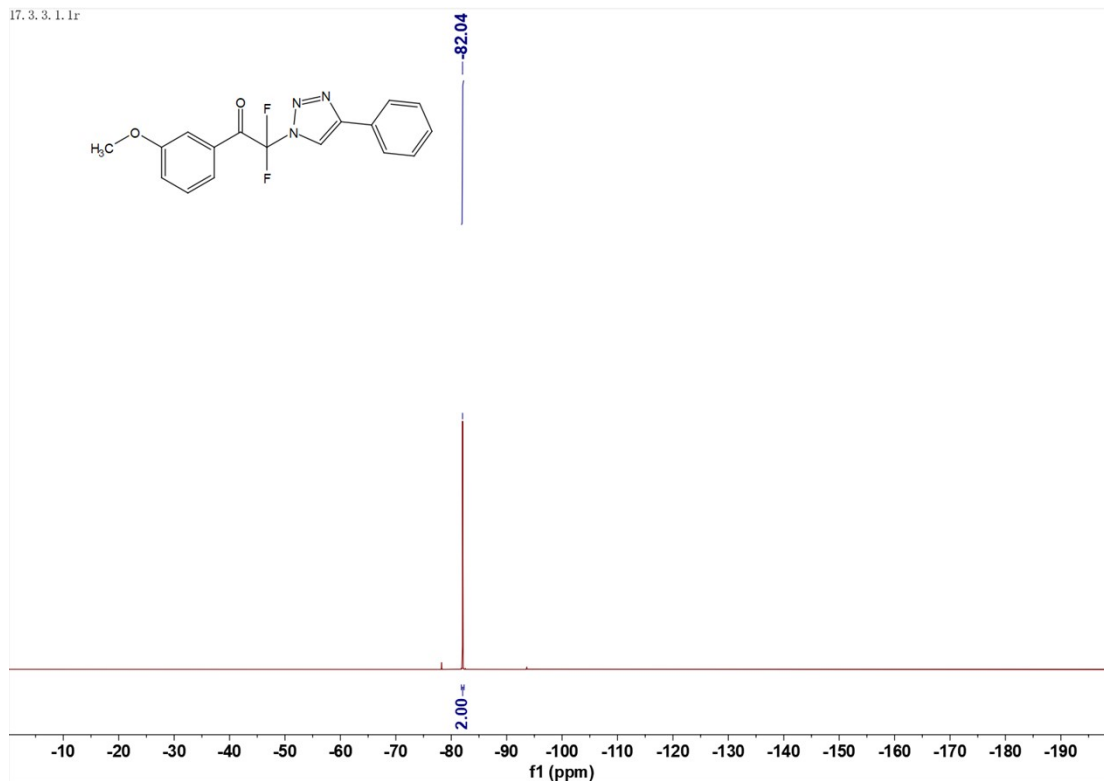


¹H NMR spectra of 4ga



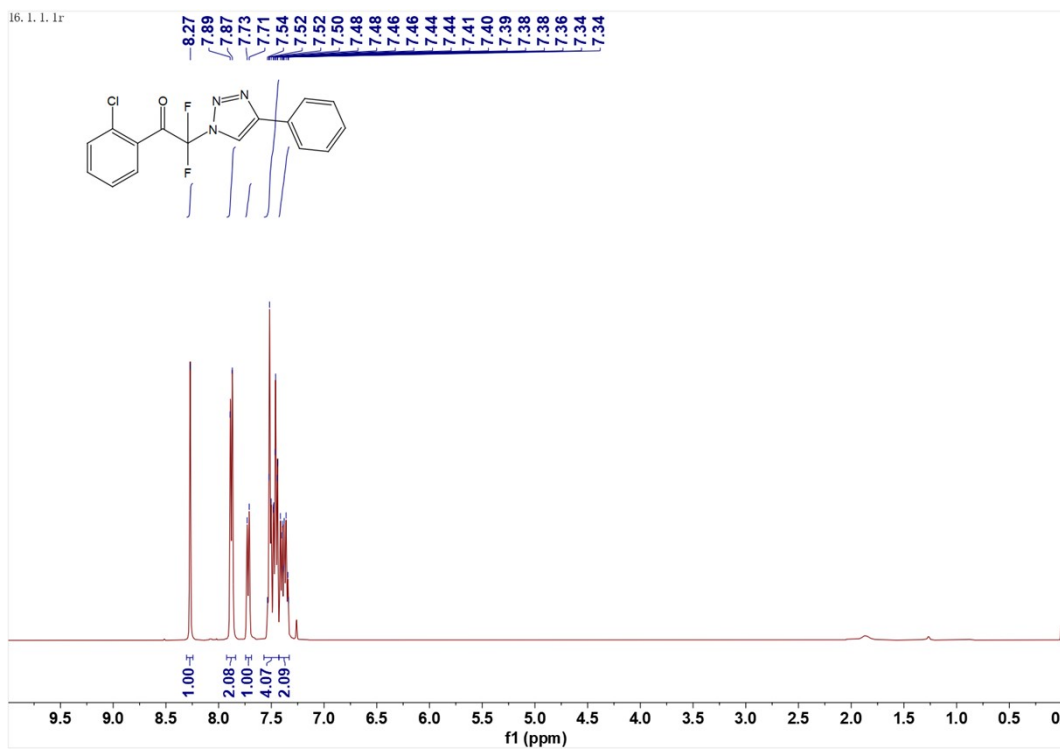
¹³C NMR spectra of 4ga

17. 3. 3. 1. 1r

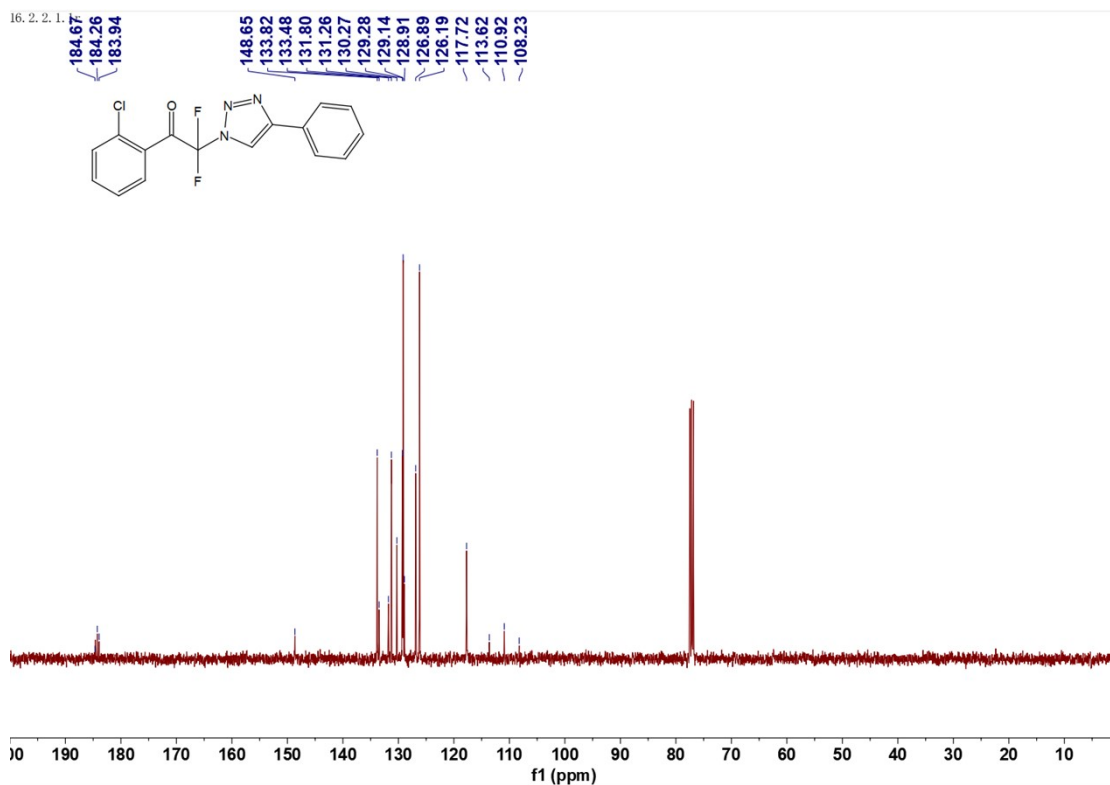


^{19}F NMR spectra of 4ga

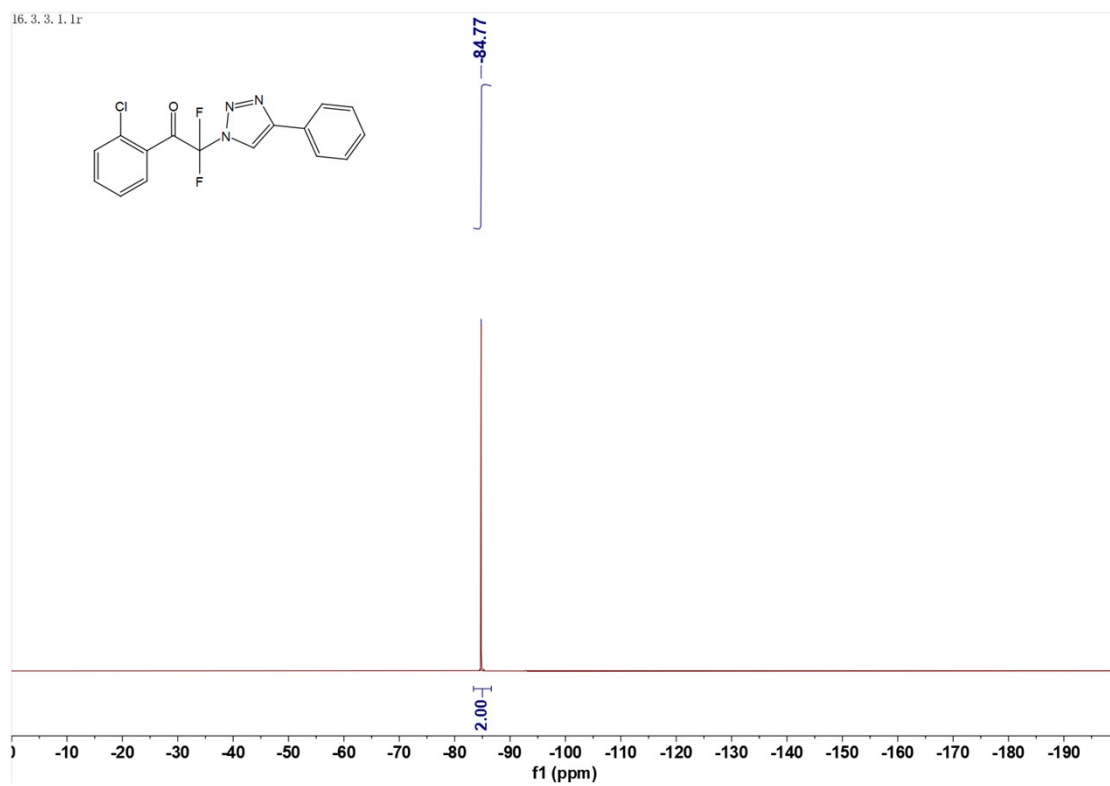
16. 1. 1. 1r



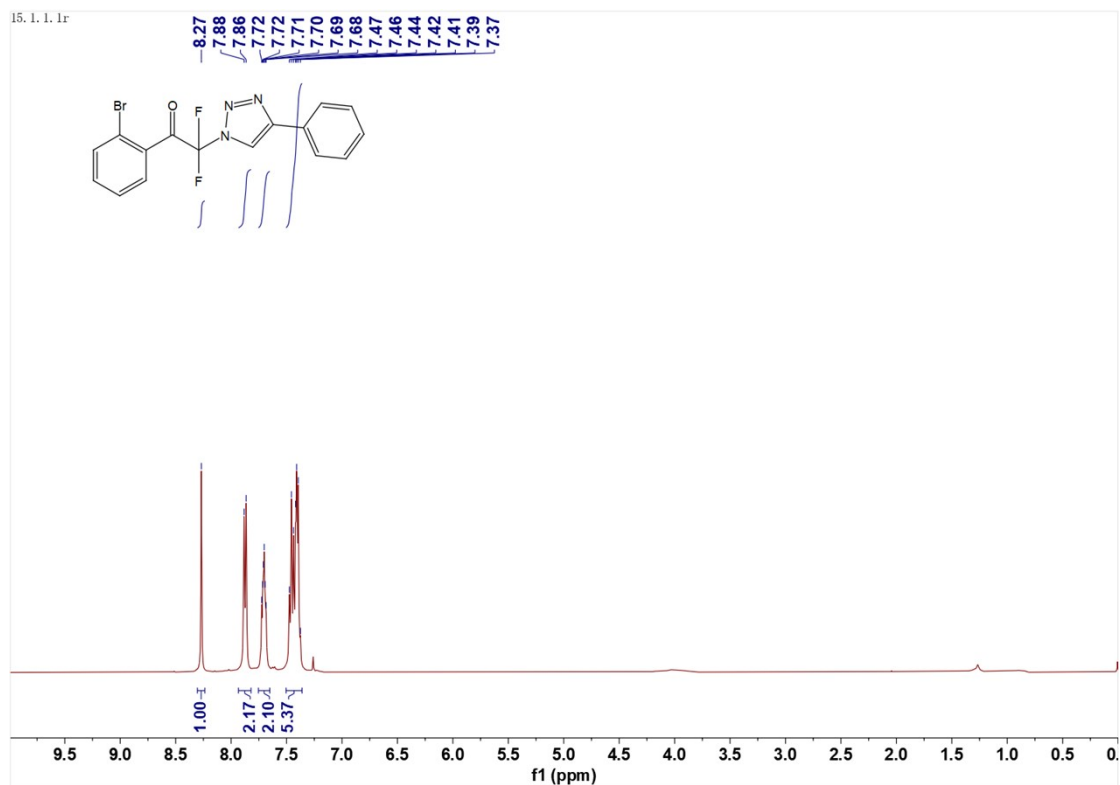
^1H NMR spectra of 4ia



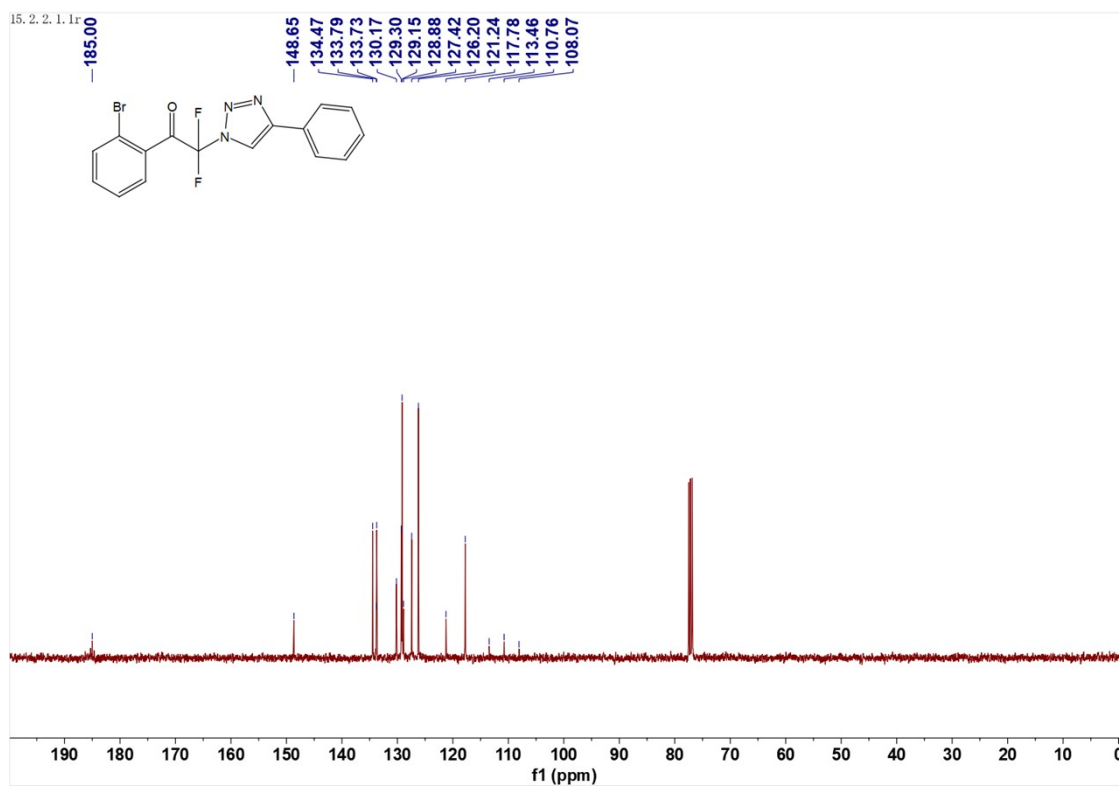
¹³C NMR spectra of 4ia



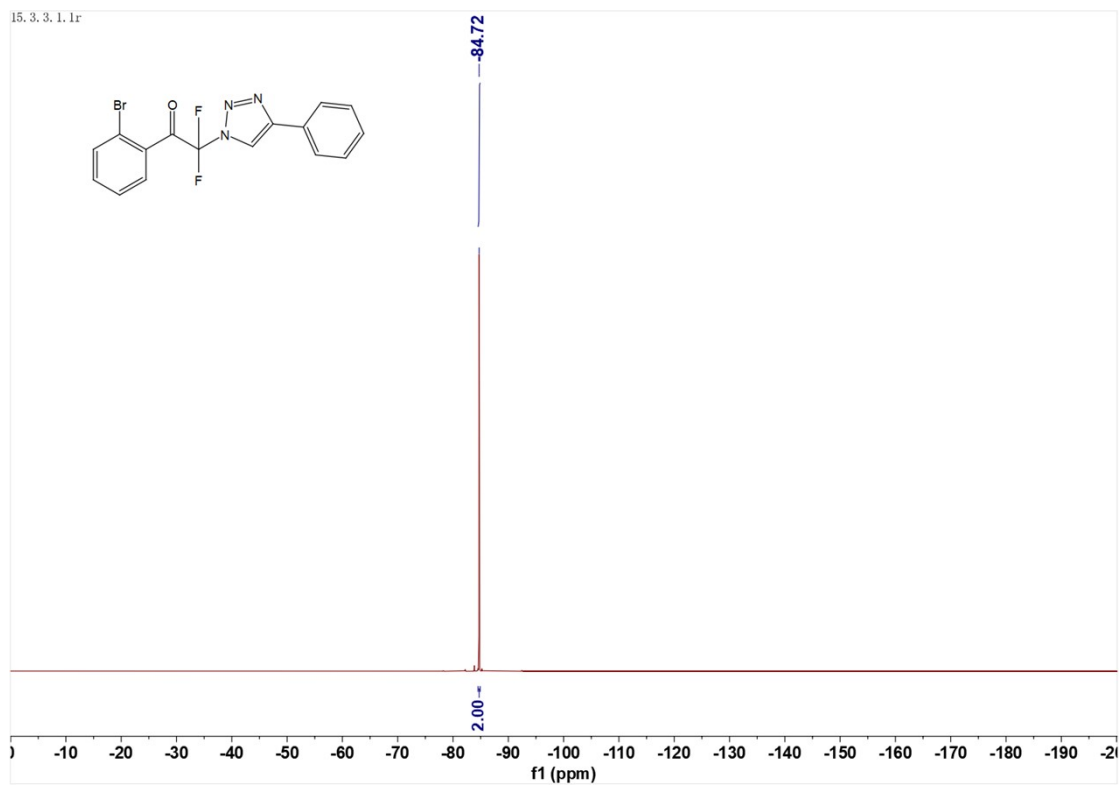
¹⁹F NMR spectra of 4ia



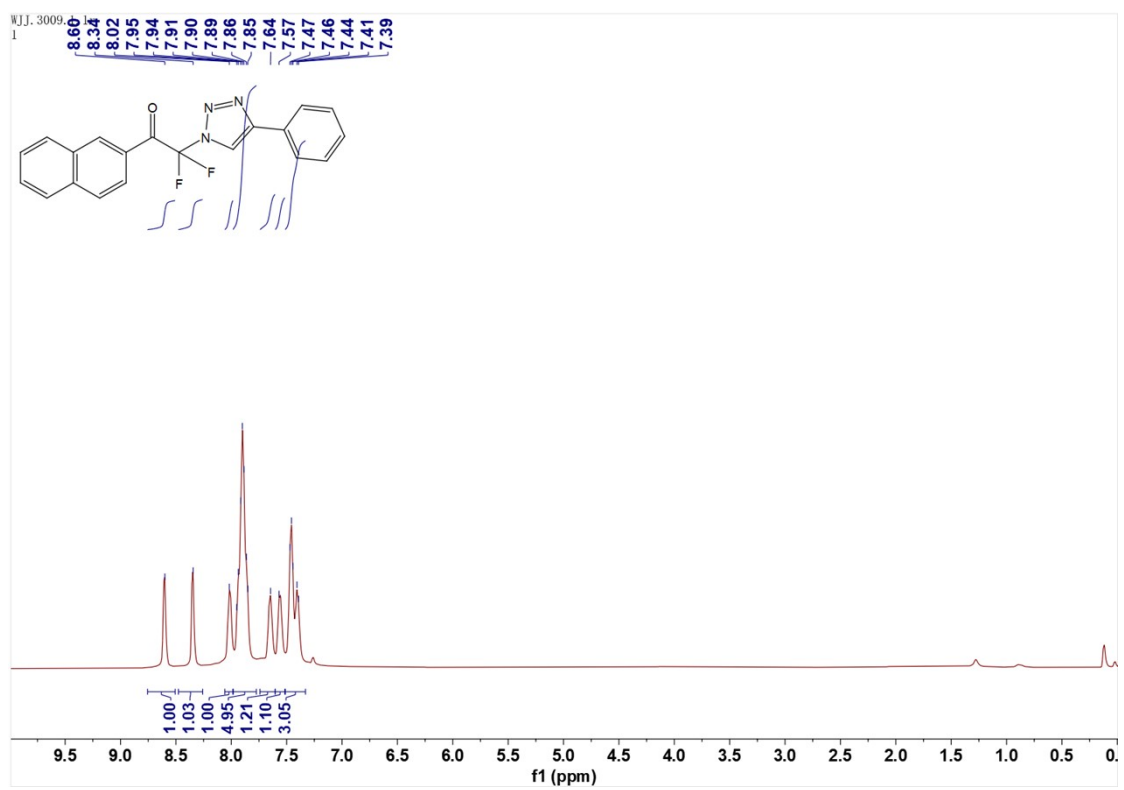
¹H NMR spectra of 4ja



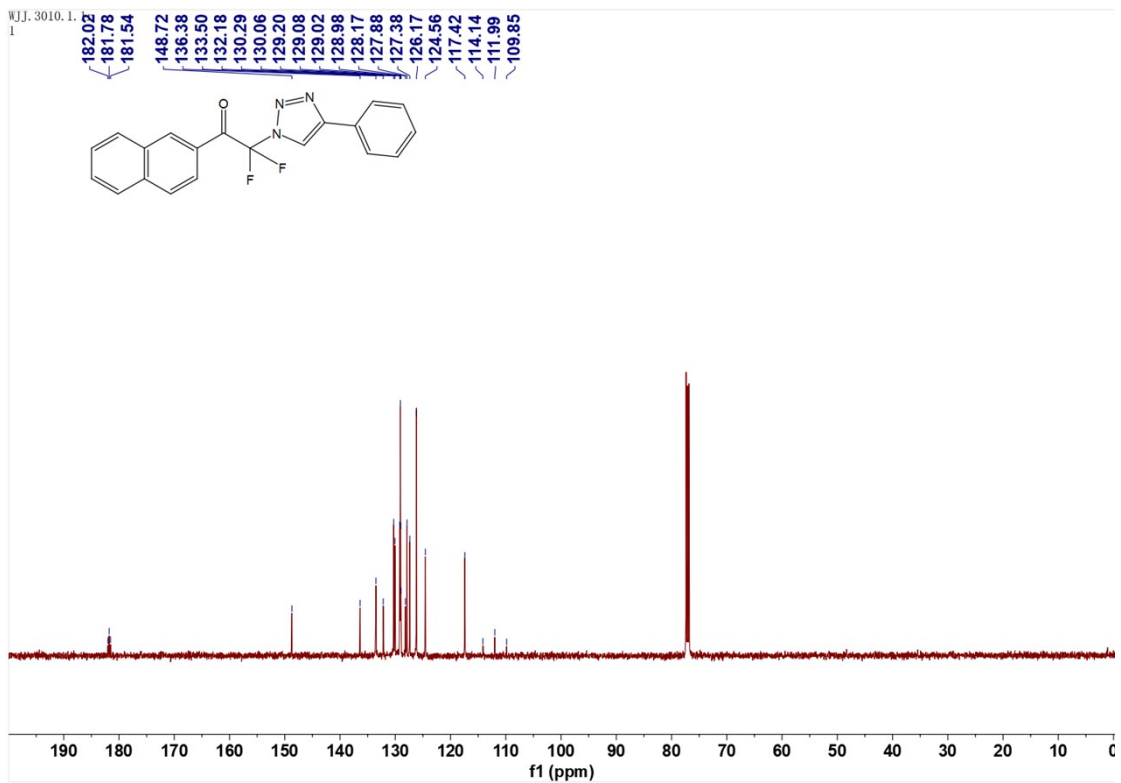
¹³C NMR spectra of 4ja



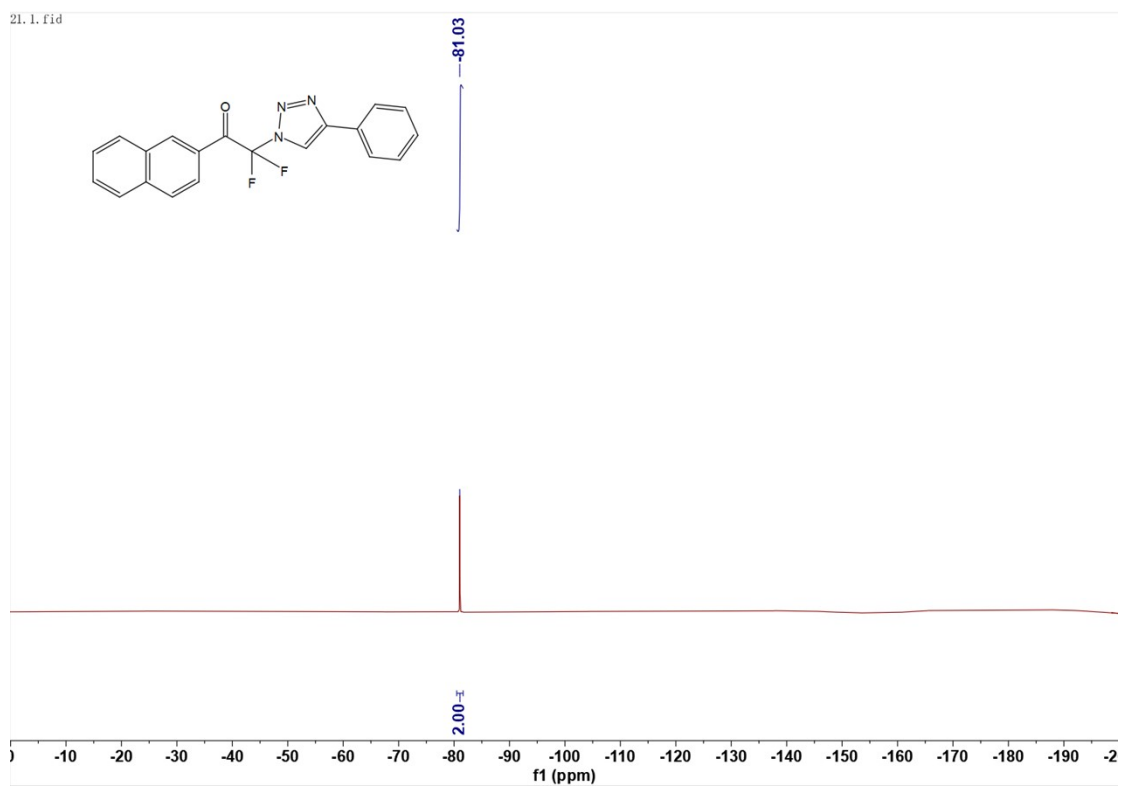
¹⁹F NMR spectra of 4ja



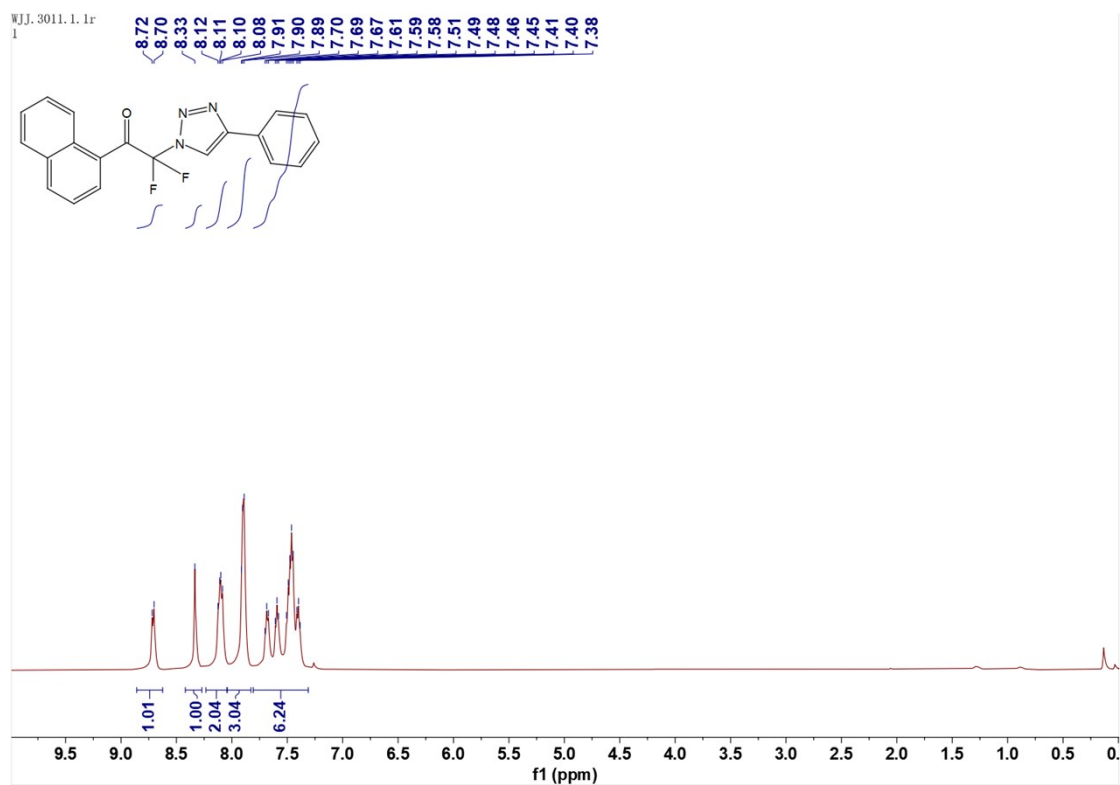
¹H NMR spectra of 4la



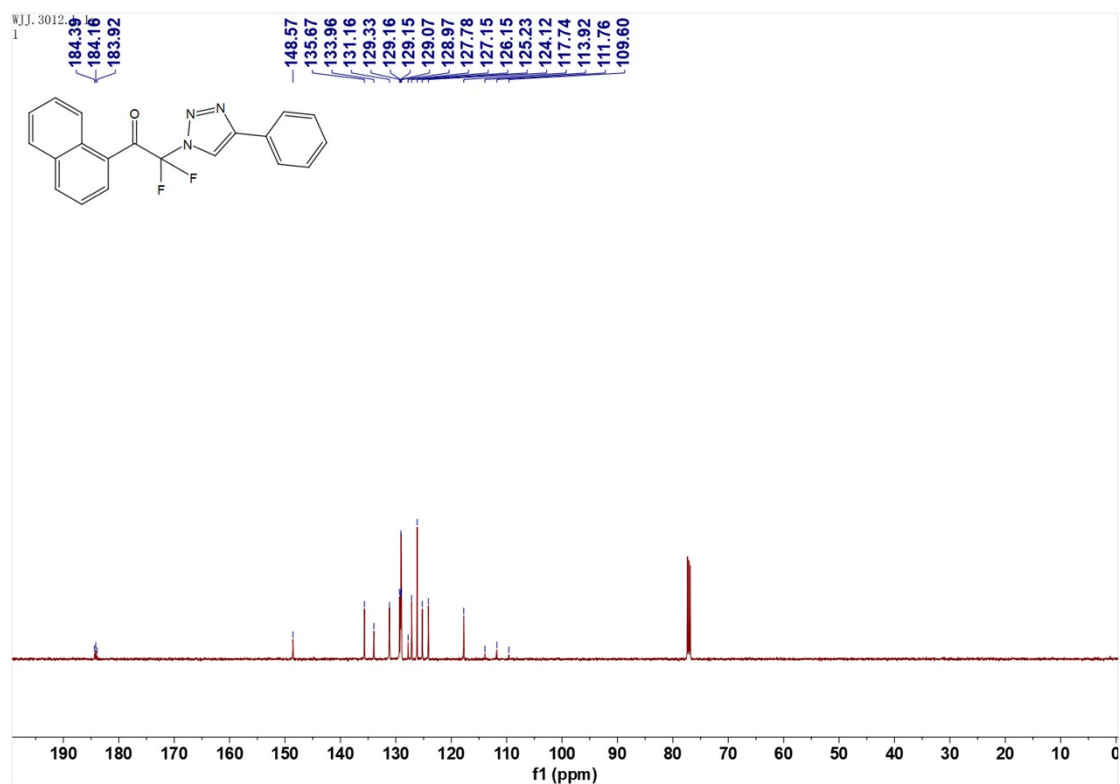
¹³C NMR spectra of 4la



¹⁹F NMR spectra of 4la

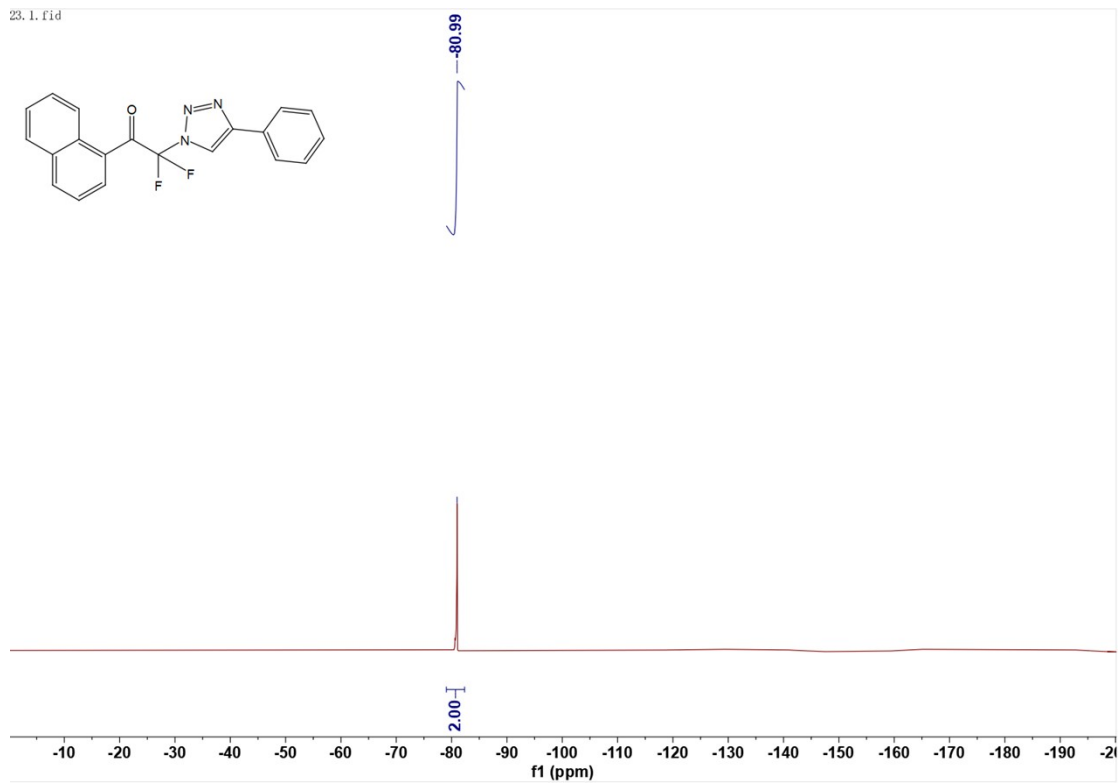


¹H NMR spectra of 4ma

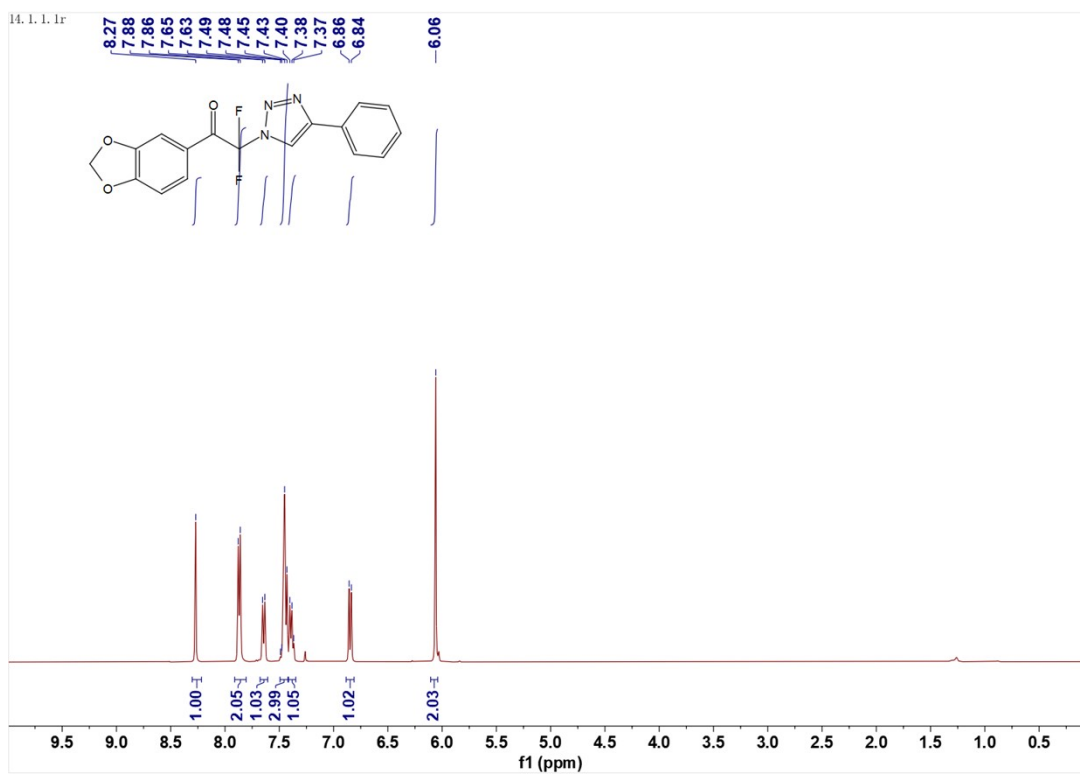


¹³C NMR spectra of 4ma

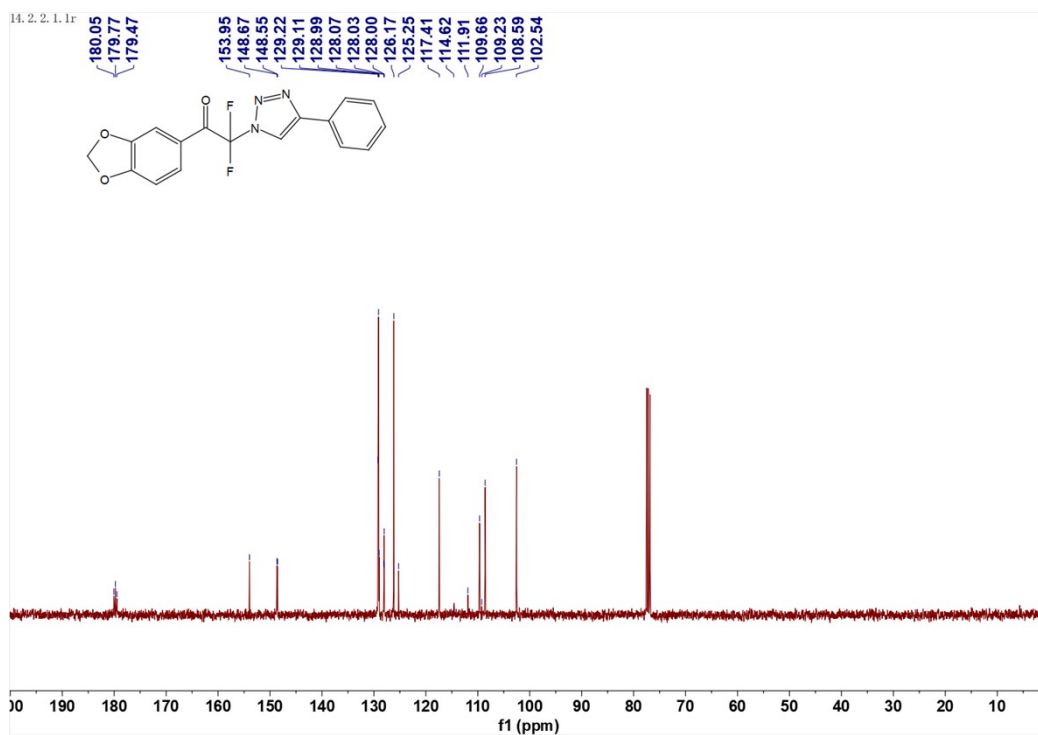
23. 1. fid



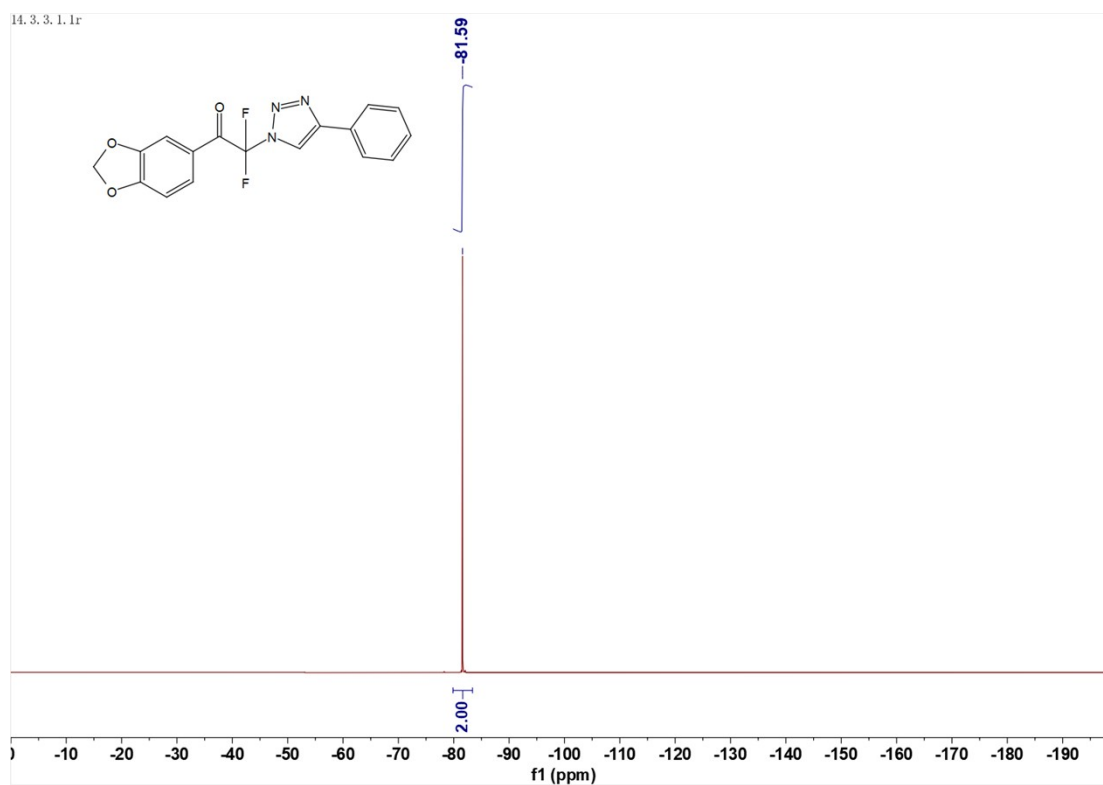
¹⁹F NMR spectra of 4ma



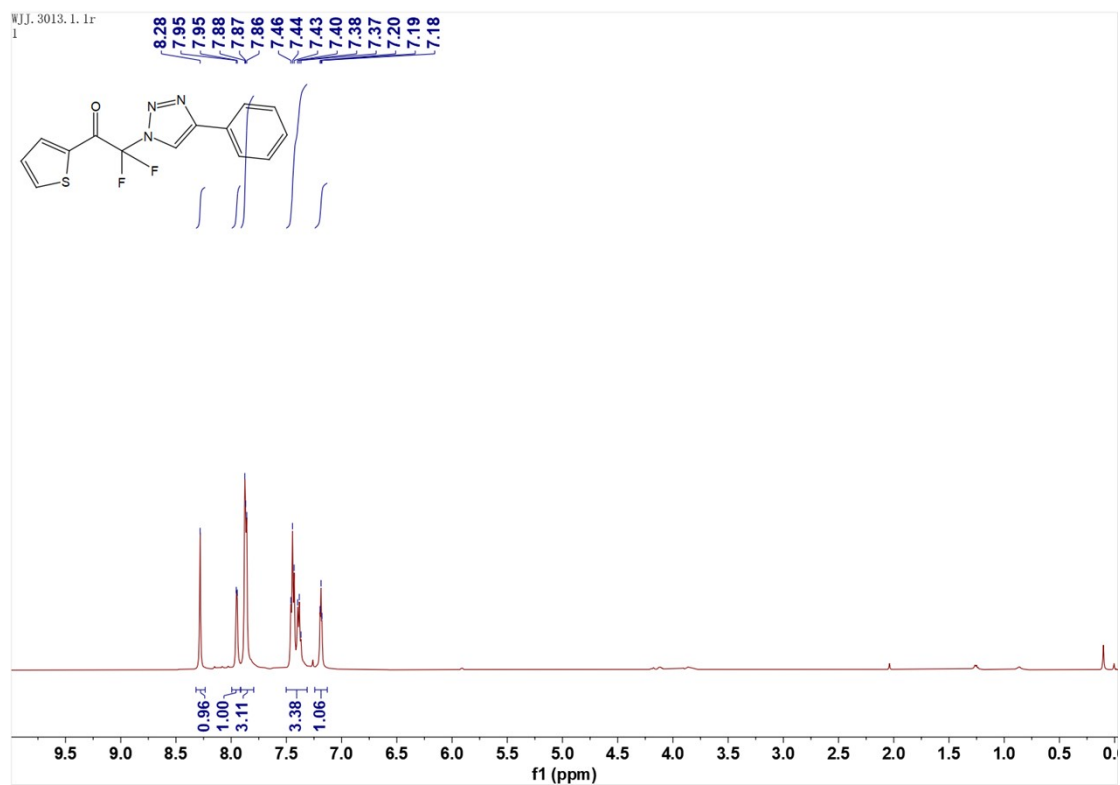
¹H NMR spectra of 4na



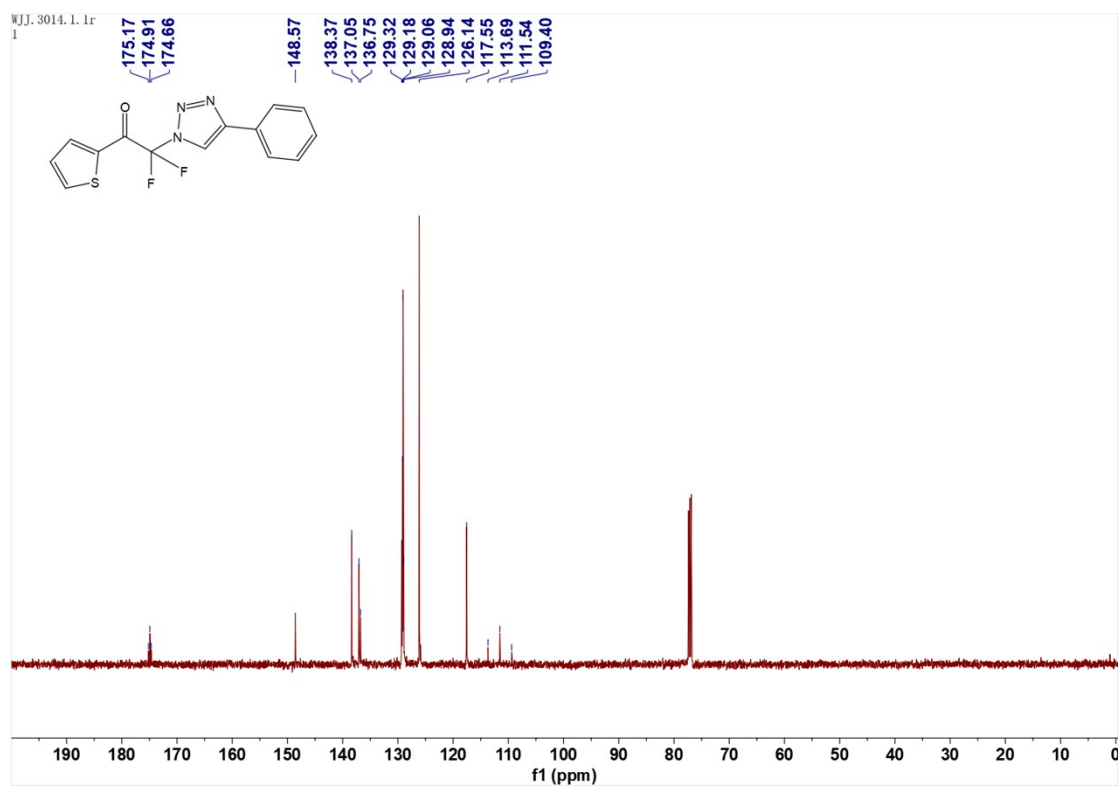
¹³C NMR spectra of 4na



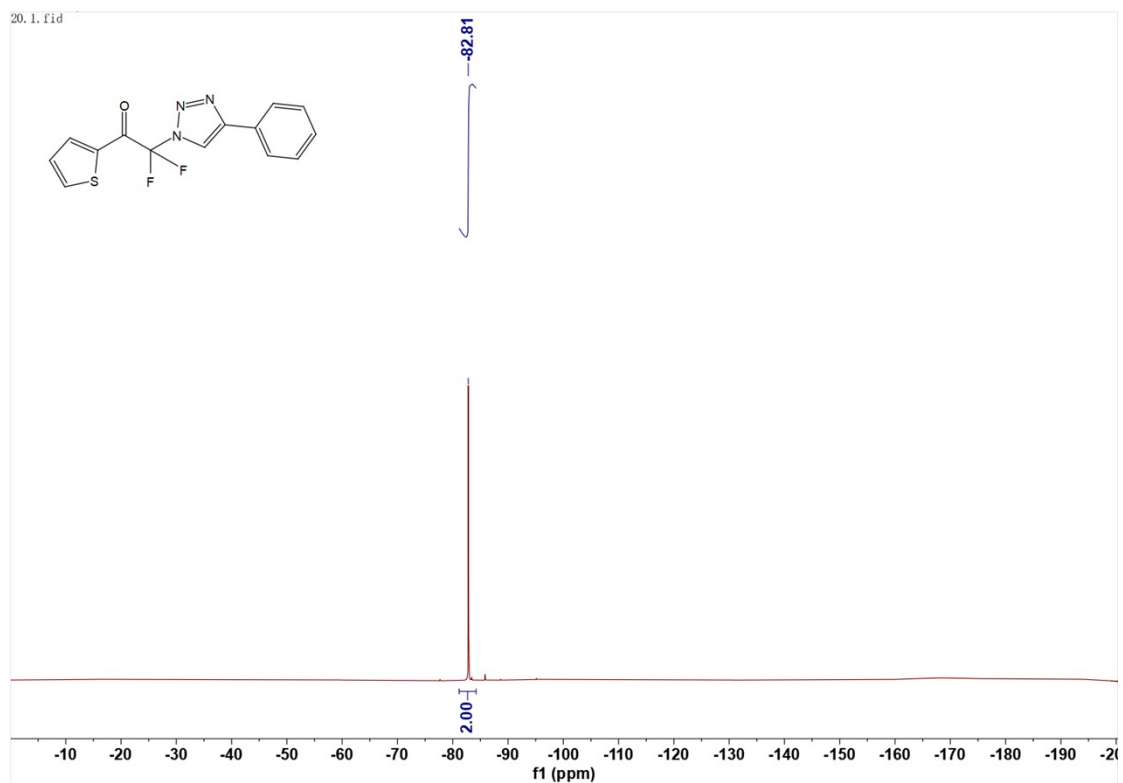
¹⁹F NMR spectra of 4na



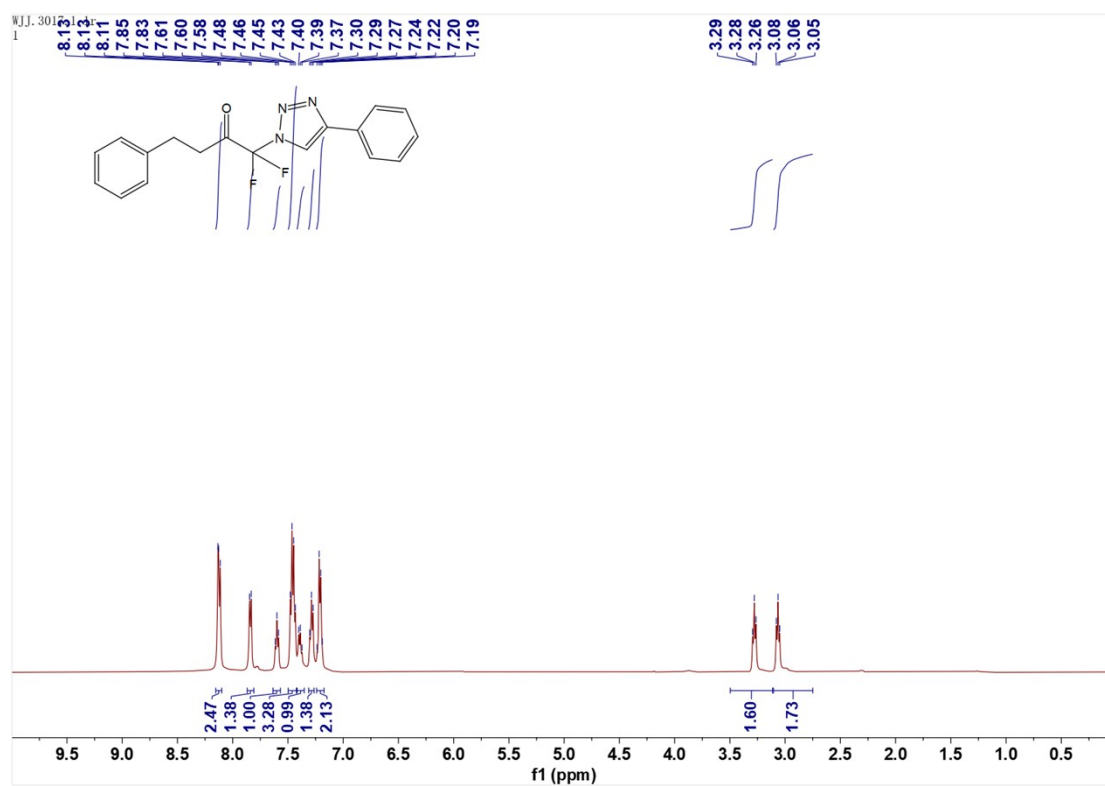
¹H NMR spectra of 4qa



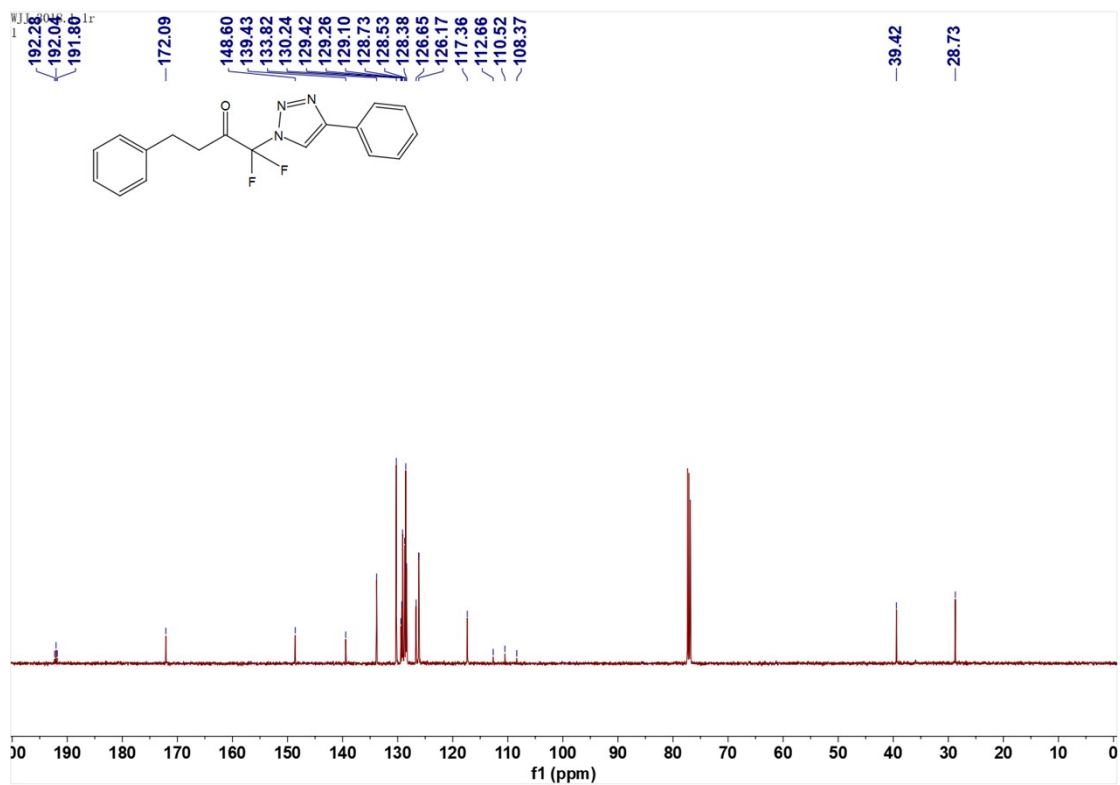
¹³C NMR spectra of 4qa



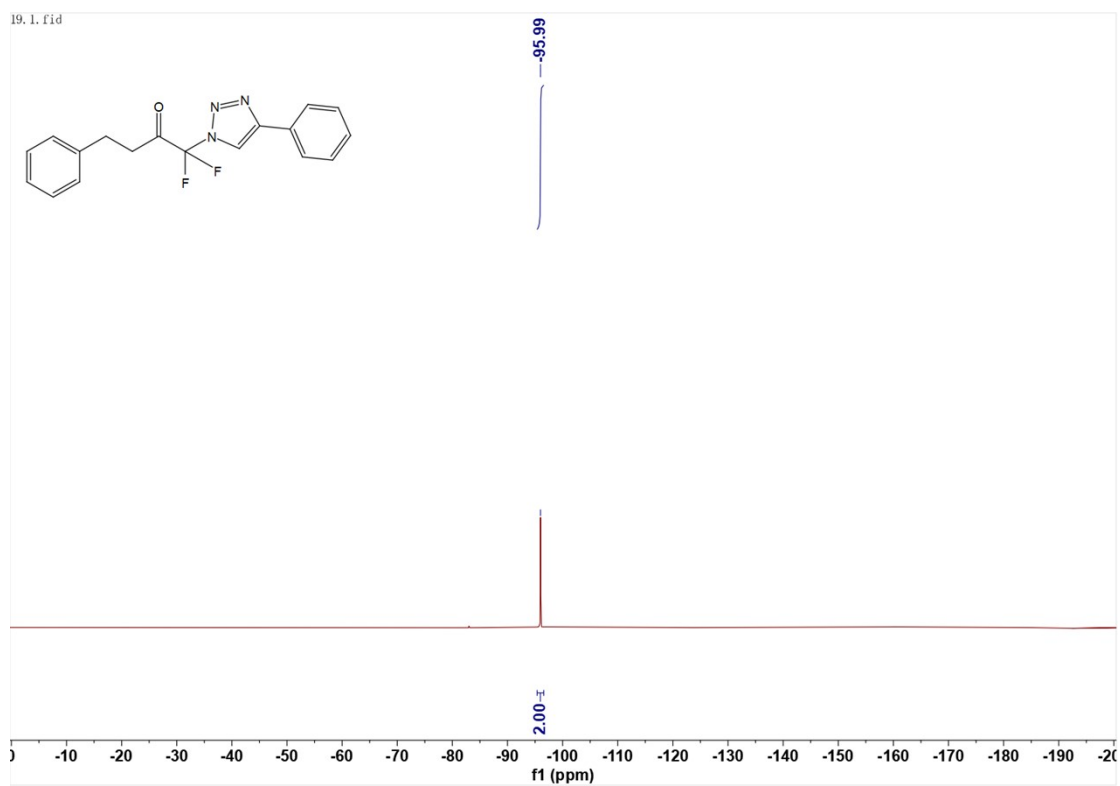
^{19}F NMR spectra of 4qa



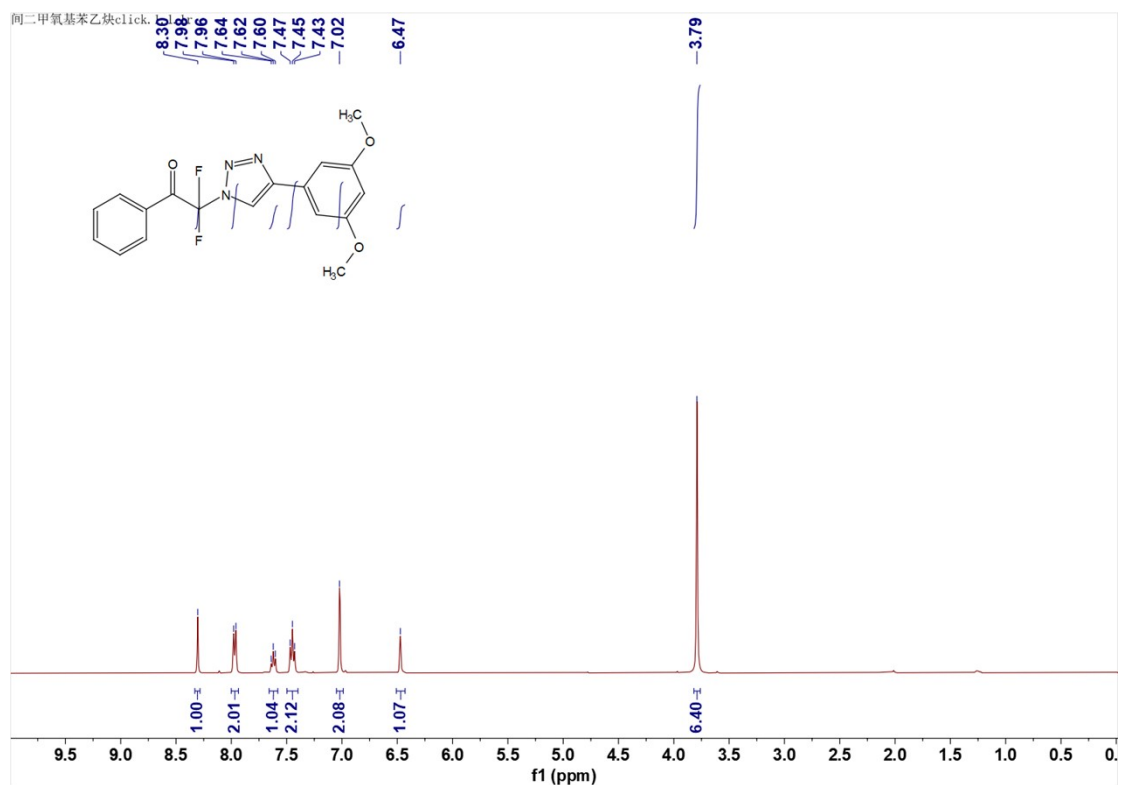
^1H NMR spectra of 4ra



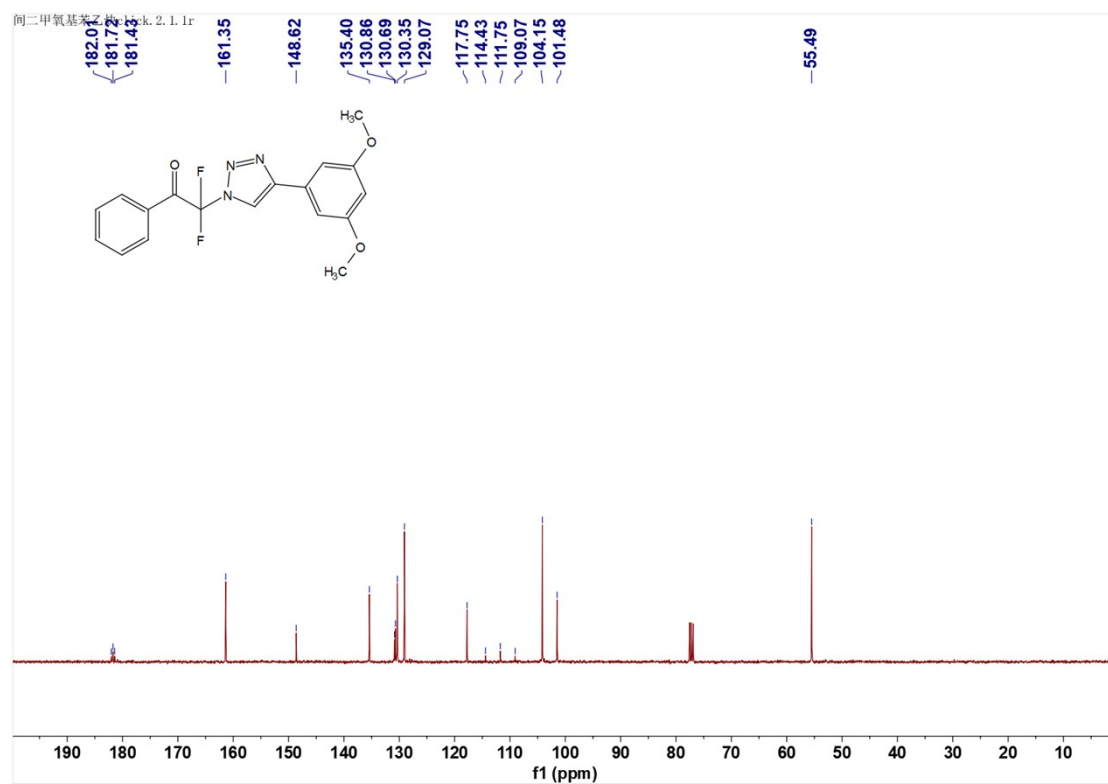
¹³C NMR spectra of 4ra



¹⁹F NMR spectra of 4ra

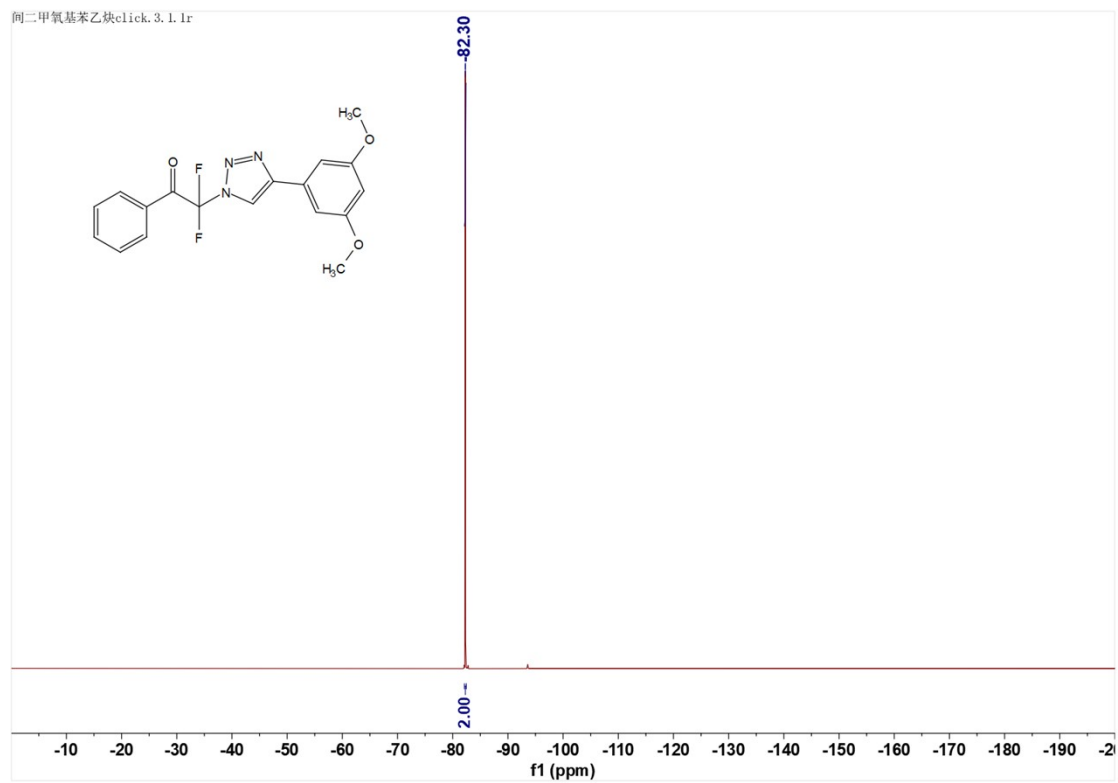


¹H NMR spectra of 4ab



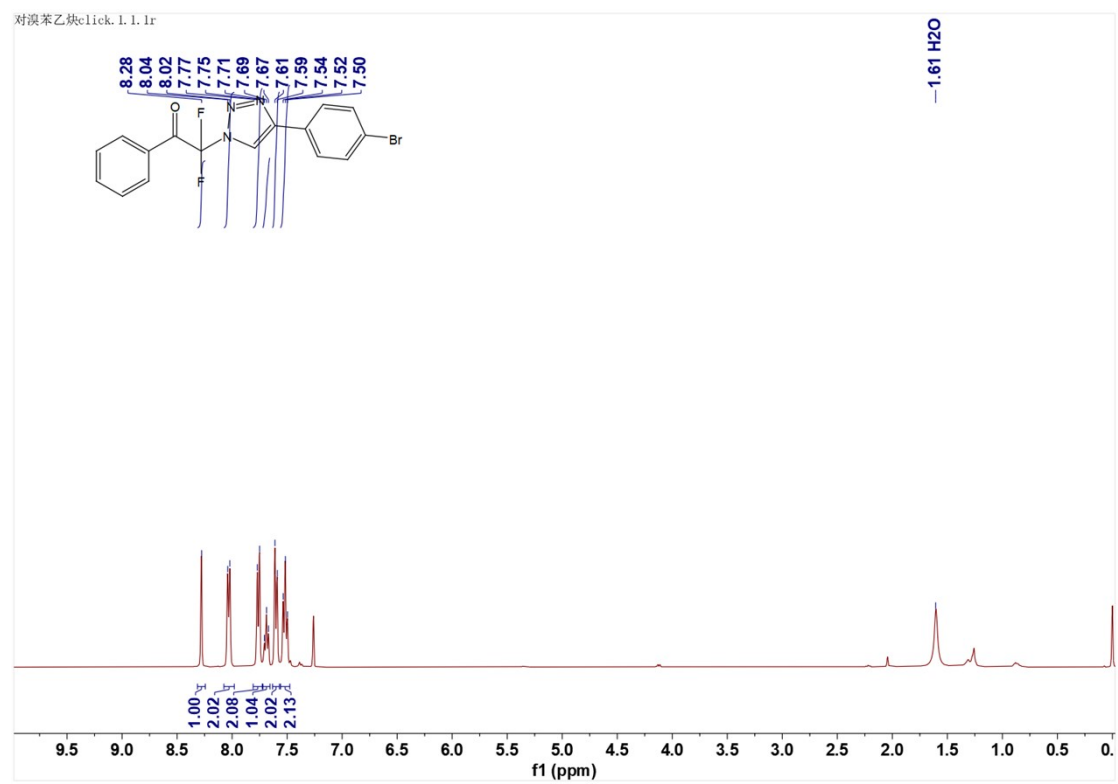
¹³C NMR spectra of 4ab

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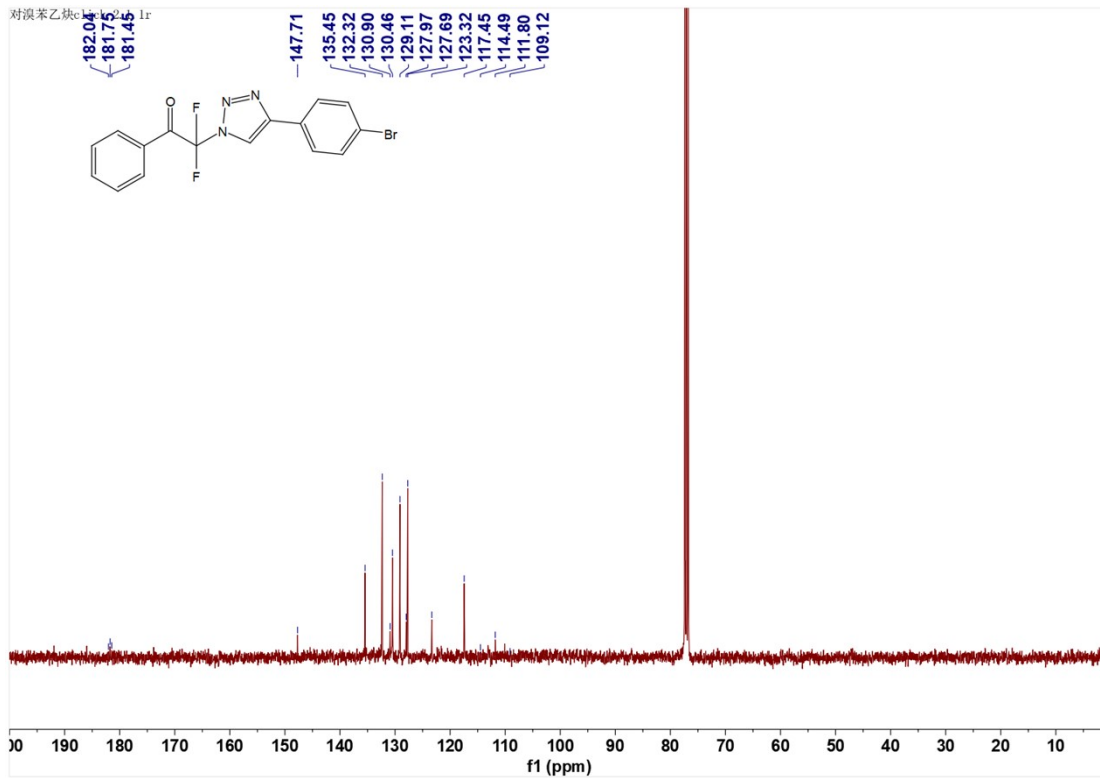


¹⁹F NMR spectra of 4ab

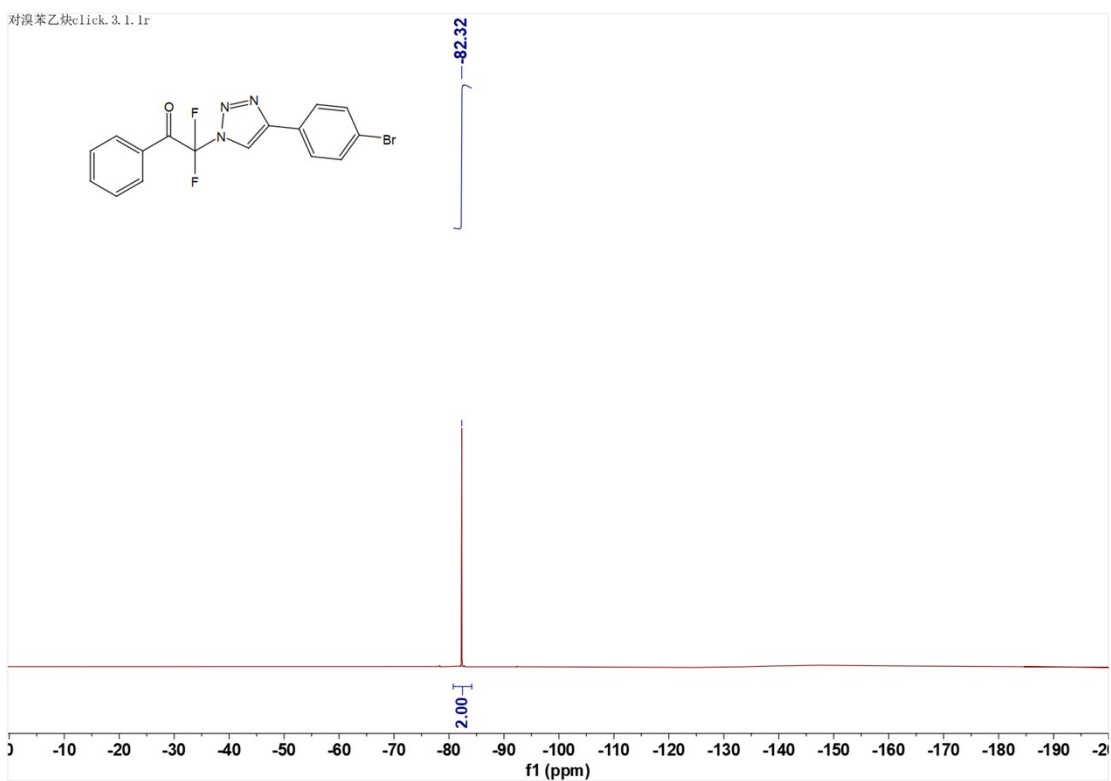
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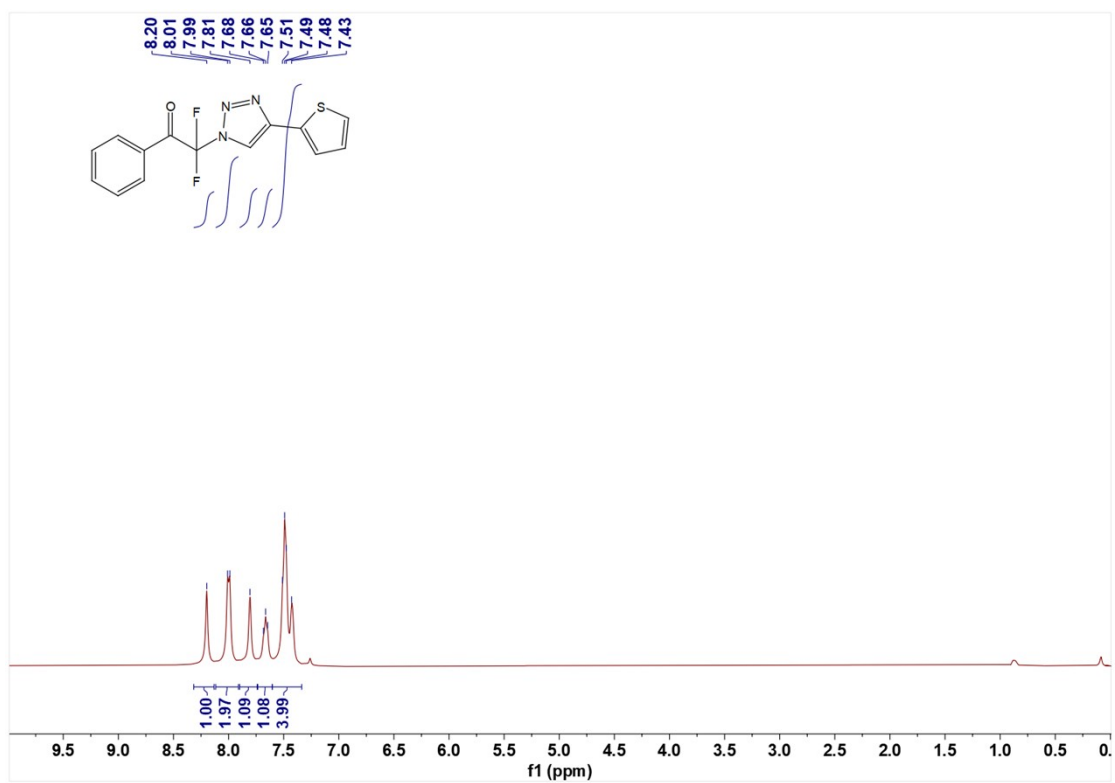
¹H NMR spectra of 4ac



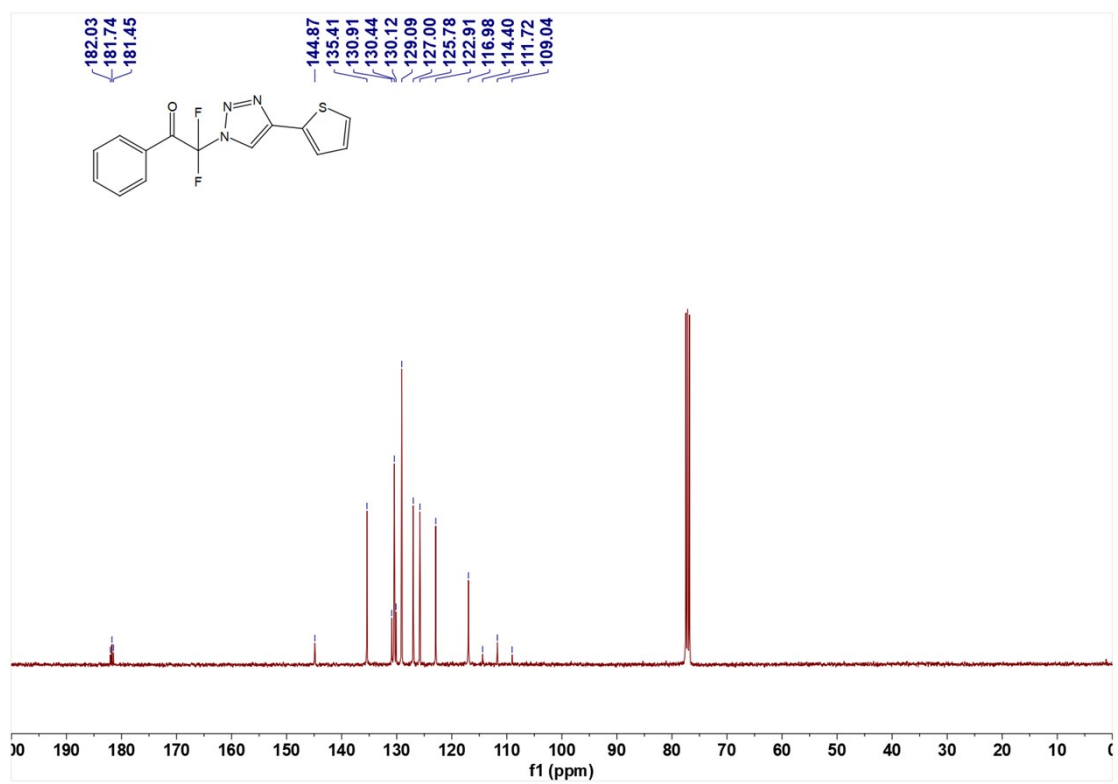
¹³C NMR spectra of 4ac



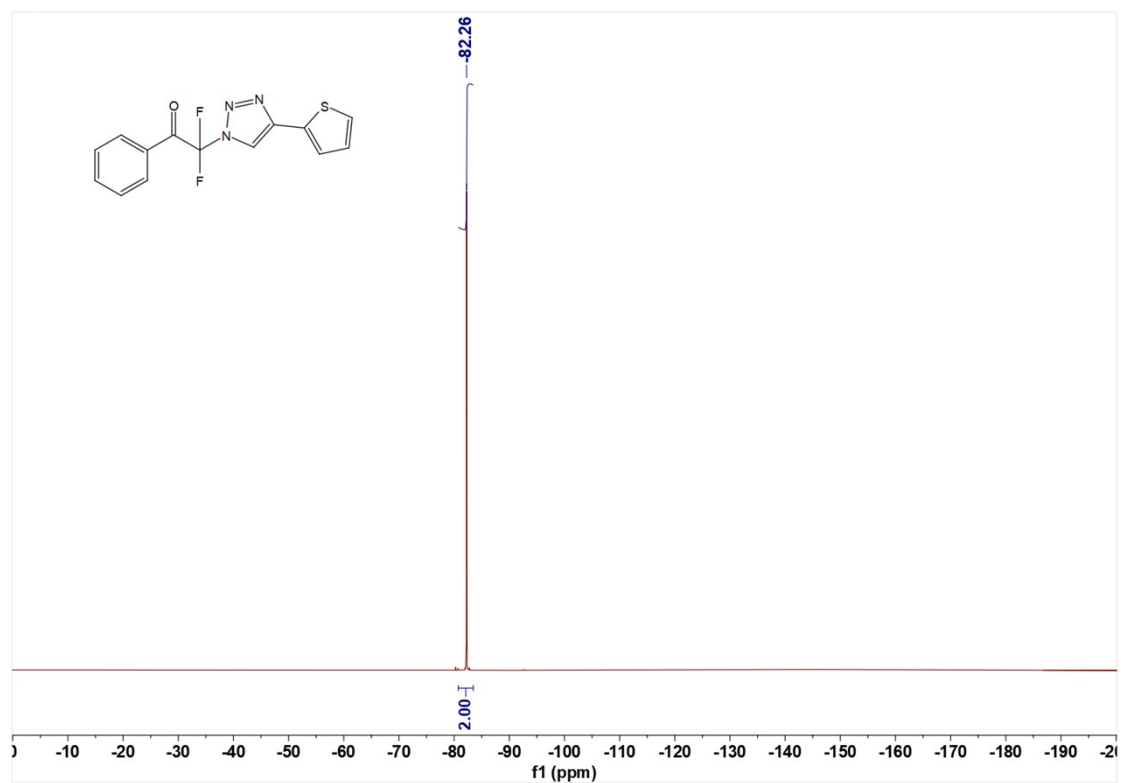
¹⁹F NMR spectra of 4ac



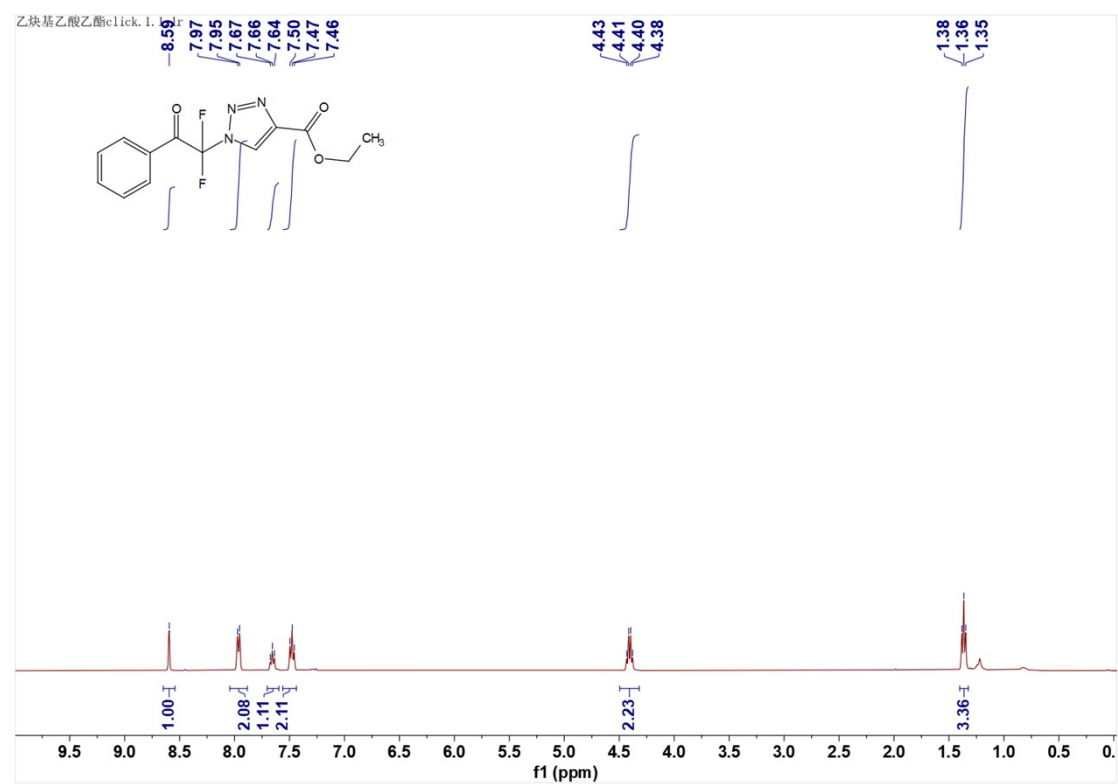
¹H NMR spectra of 4ad



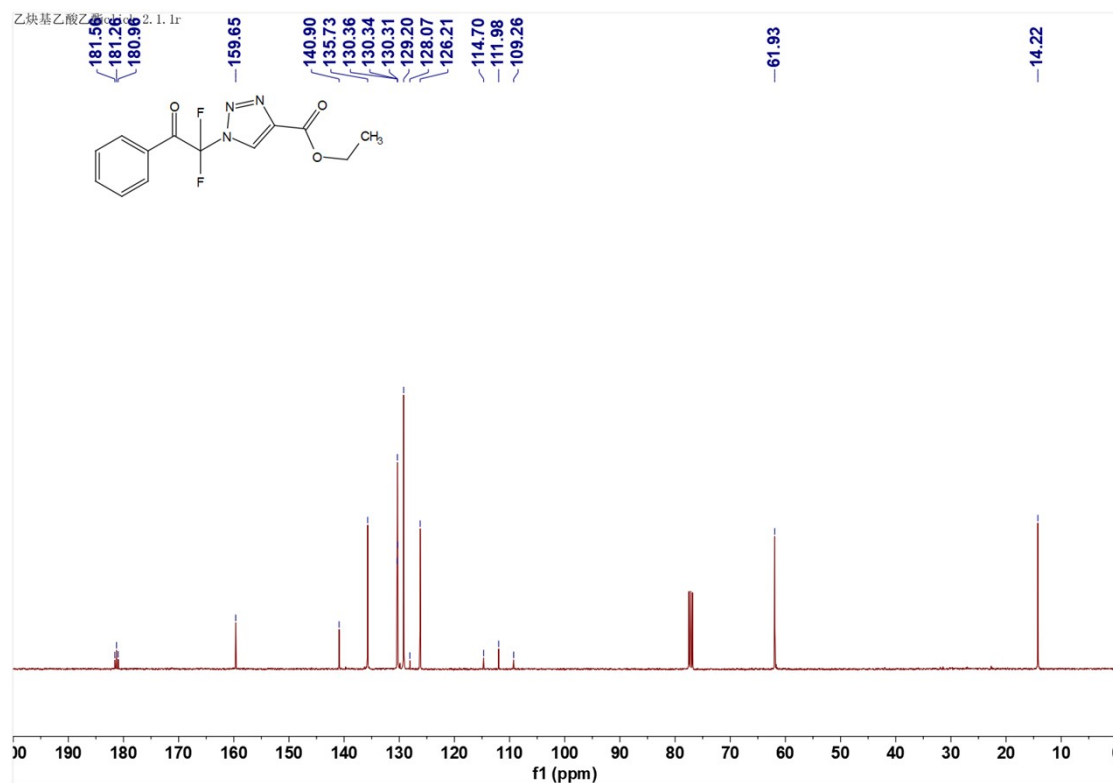
¹³C NMR spectra of 4ad



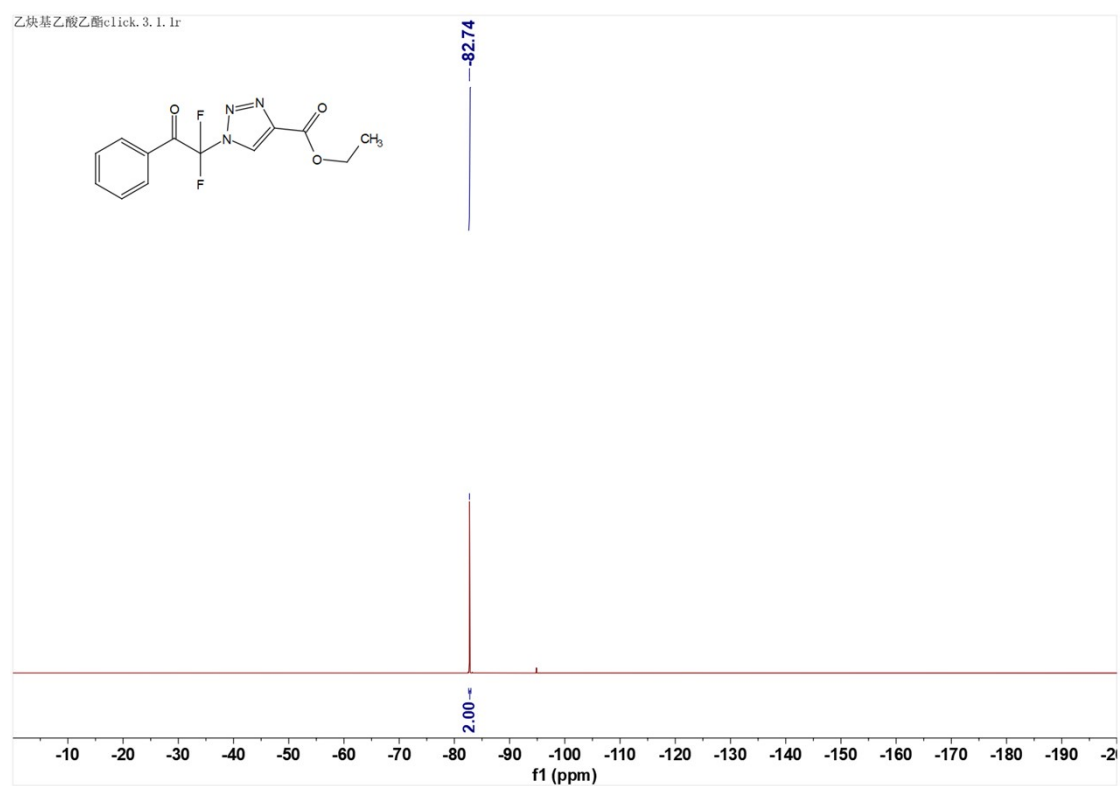
^{19}F NMR spectra of 4ad



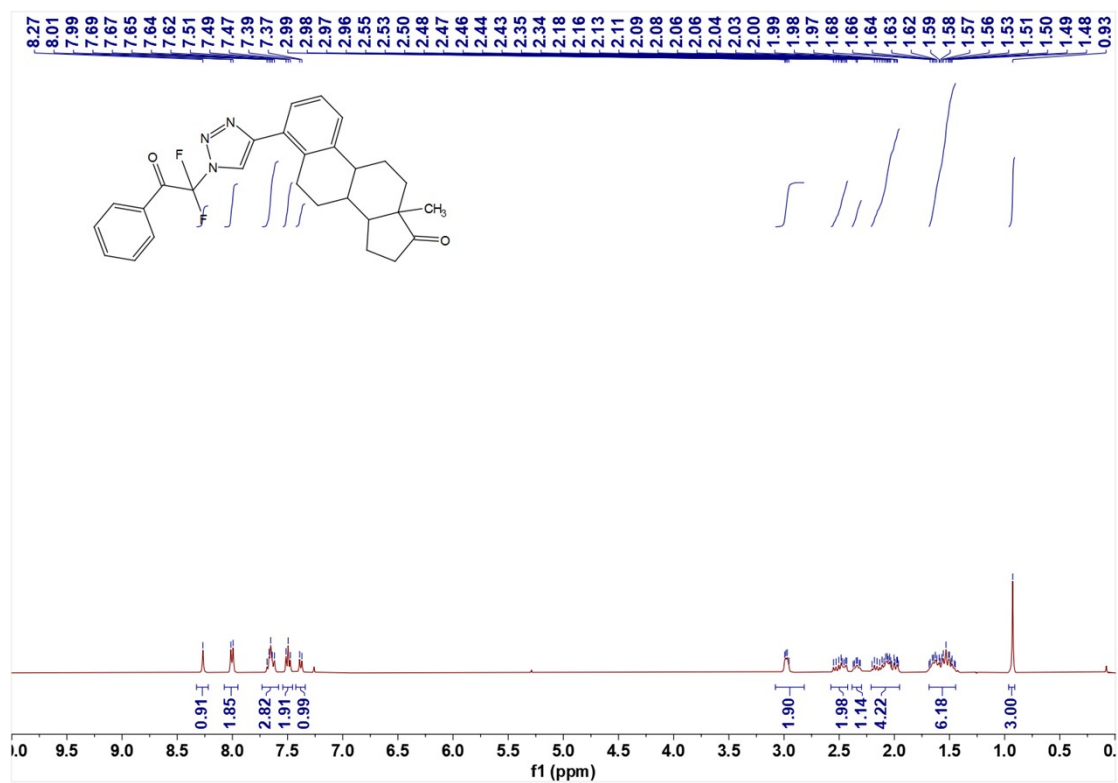
^1H NMR spectra of 4ae



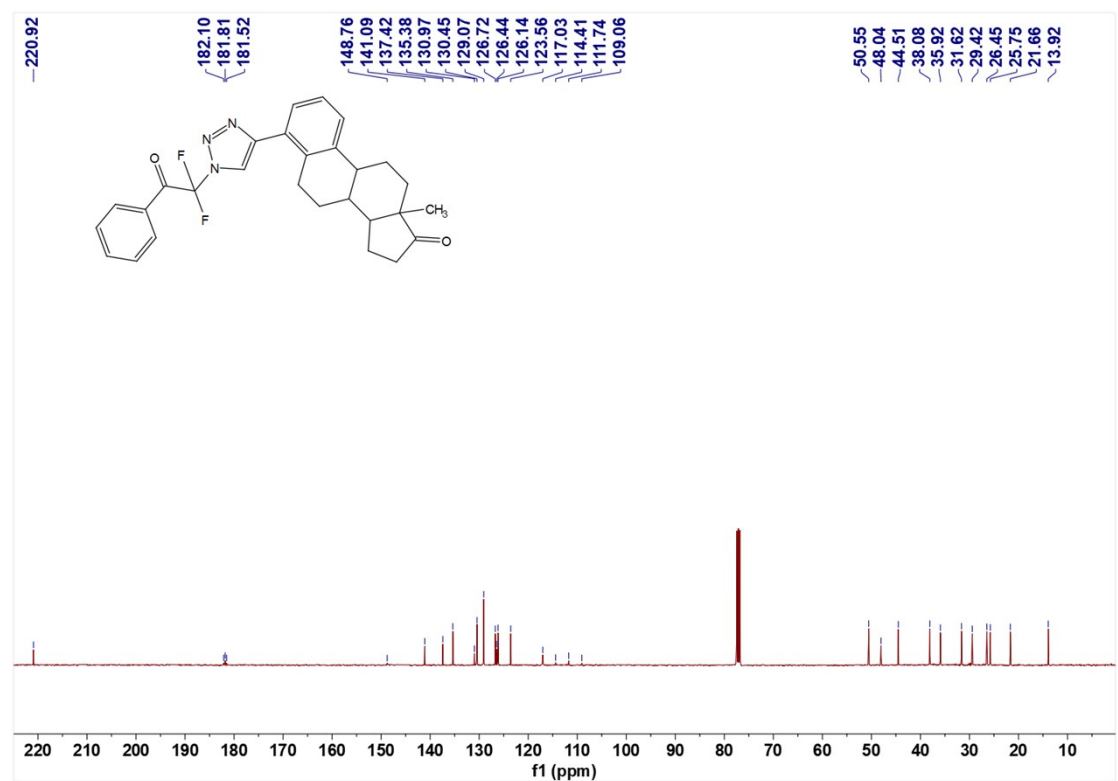
¹³C NMR spectra of 4ae



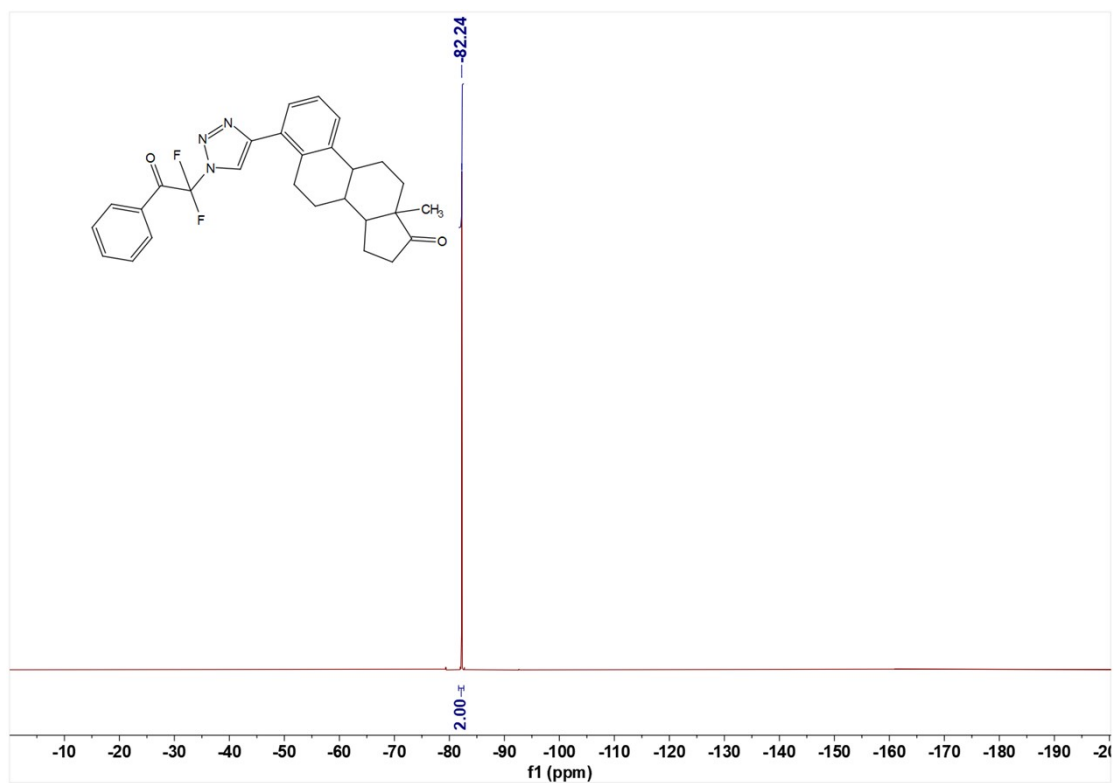
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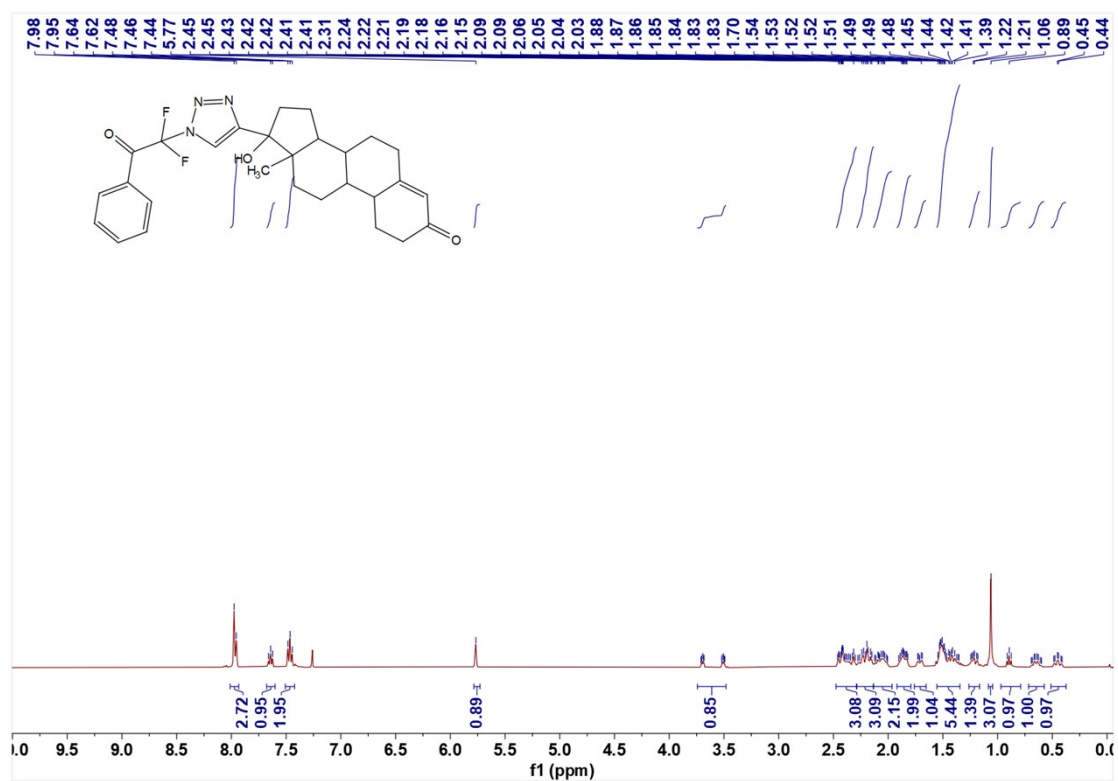
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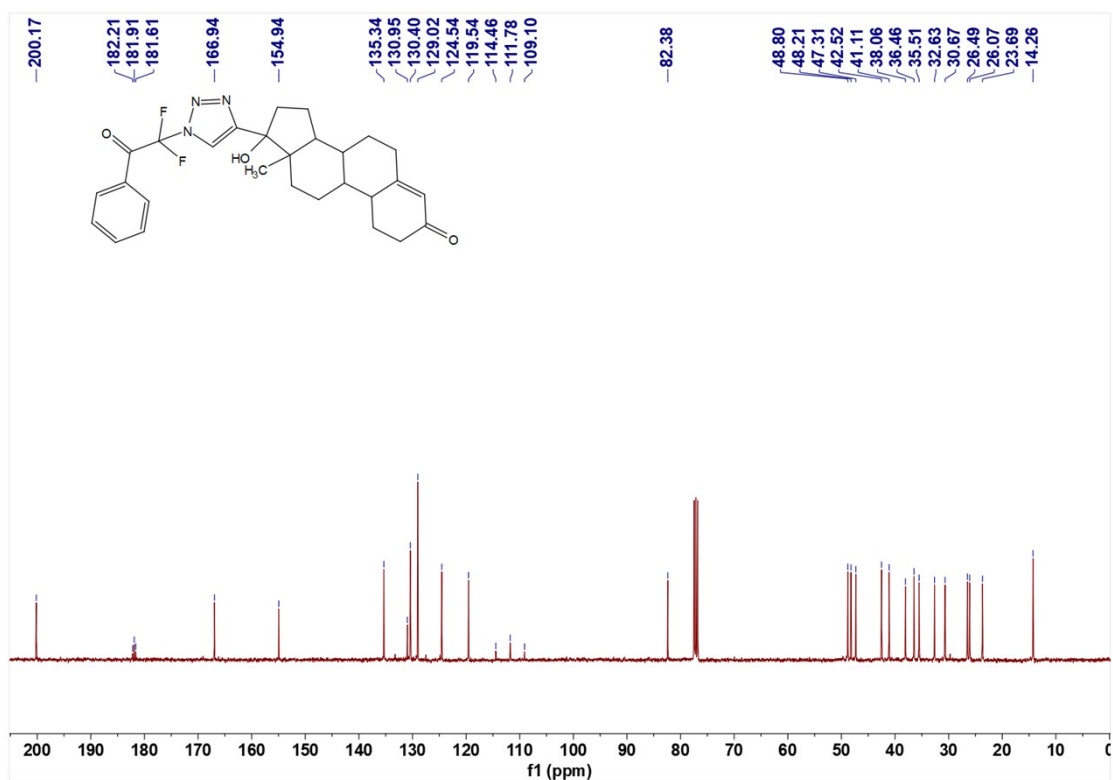
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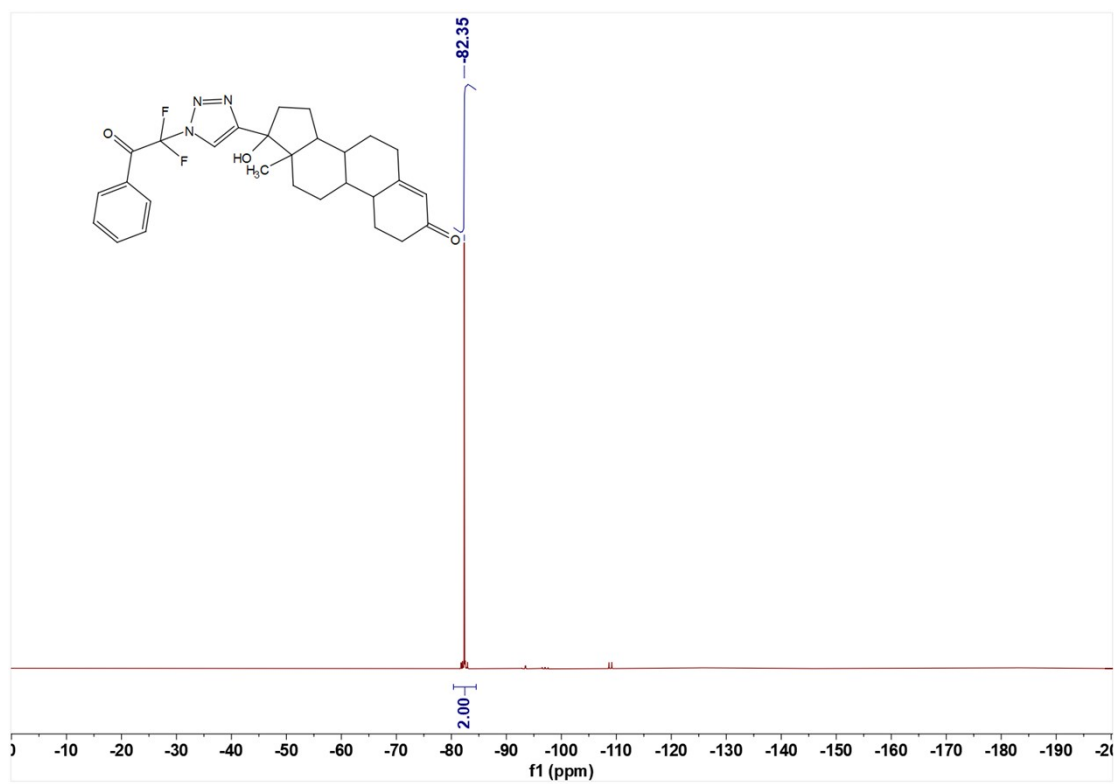
¹⁹F NMR spectra of 4af



¹H NMR spectra of 4ag



¹³C NMR spectra of 4ag



¹⁹F NMR spectra of 4ag

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